CHROMATE SORPTION ON METAL IONS DOPED GOETHITE (\(\alpha\)-FeOOH)

BY

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UNIVERSITY OF PESHAWAR
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GOETHITE (\(\alpha\)-FeOOH)

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EXTERNAL EXAMINER
INTERNAL EXAMINER
DEDICATED

To my parents whose spiritual
love always kept me determined.

SADULLAH KHAN
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SADULLAH KHAN
Abstract

Goethite (α-FeOOH), being a model adsorbent, has a very highly reactive surface. Therefore, it is considered to be an efficient adsorbent in soil systems and plays an important role in controlling the mobility of trace contaminants, like Pb, Ni, Cu, Cr, As, Cd, Co, Zn, and Cu etc. Being the most abundant iron oxide mineral in almost all the soil types, many researchers have focused, recently, on the sorption properties of metal doped goethite, not only due to its greater resemblance with natural goethite, but also for its possible use as an adsorbent in water purification technology.

In line with this trend of research, the present study reports the characterization of Pb, Ni and Cu-doped goethite and their adsorption properties for chromate with stepwise comparison to pure goethite. Further, characterization and chromate adsorption properties of microcrystalline and amorphous phases of copper/iron mixed oxides, are also a part of this study. All the solid samples, used in the present investigation, are prepared according to a well known procedure reported in the literature. The amounts (%) of Pb\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\) ions doped in goethite samples were 0.38, 0.25 and 0.32, while the microcrystalline goethite and amorphous phases of copper/iron mixed oxides contained 6.27 and 11.31% Cu\(^{2+}\) ions respectively. All these solids are characterized for Surface Area, pH of Point of Zero Charge (pH\(_{\text{pzc}}\)), XRD, TG-DTA, TEM/SEM and FTIR analyses.

XRD and TEM/SEM analyses of all the goethite samples suggest the solids to be crystalline and doping of the metal ions have only slightly affected the unit cell parameters of the crystals. TG-DTA analyses reveal that all the goethite samples exhibit similar thermal behavior with a distinct peak for the degradation of doped metal hydroxides, present in the solid matrix.. Furthermore, an increase in the concentration of Cu in the precipitate results in the formation microcrystalline goethite and amorphous phase of copper/iron mixed oxide with a marginal increase in the surface area and pH\(_{\text{pzc}}\) of the resultant solid phases.
Dissolution study of goethite in KNO₃ and 303K suggest that goethite and its metal doped counterparts are quite stable in the pH range 4-7. In all the solid samples dissolution is maximum at the lowest pH of 3 and decreases with the increasing pH. Dissolution of pure goethite is inhibited by increasing the concentration of chromate, while in the metal-doped goethites, it has no effect on their dissolution. The amorphous and microcrystalline mixed oxides of copper/iron also observed to follow the dissolution behavior of metal doped goethites.

Adsorption studies of chromate suggest that doping of metal ions increases the chromate adsorption capacity of goethite from 62.8 to 72.2% for Pb, from 61.4 to 82.92% for Ni and from 64.4 to 84.5 for Cu doping in it. The adsorption studies carried out at pH 3, 5 and 7 suggest that the adsorption of chromate is maximum at low pH values and decreases with increasing pH by all the solid samples used here. The effect of temperature is, however, different for different samples. In case of Pb and Cu-doped goethite, an increase in temperature decrease the adsorption capacity of the solid, while for all the other samples adsorption capacity is observed to increase. The amorphous copper/iron mixed oxide sample has been found to be the best adsorbent for chromate of all the solids used in the present investigation.

The values of isosteric heat of adsorption, calculated from the Clausius Clapyron Equation, are positive for Ni doped goethite and negative for Cu and Pb-doped goethite. In case of amorphous phases of copper/iron mixed oxides these values are also found to be positive. The values of isosteric heat of adsorption for chromate adsorption by all the solids are consistent with the effect of temperature determining the endothermic/exothermic nature of the surface reactions. Langmuir equation is applicable to the data under all the experimental conditions. The constants of this model calculated for the adsorption of chromate by all the
solids coincide well with the adsorption capacity of the respective solids obtained from the experimental data.

TEM/SEM analyses suggest that doping of foreign elements in the iron oxide structure, not only increases the sizes of the solid particles, but also increase their surface roughness. Theses changes in the solid particles result in an increase in the surface area, $\text{H}^+/\text{OH}^-$ ions adsorption capacity and hence increase the net surface positive charge. These changes collectively increase the adsorption capacity of the doped solids. FTIR analyses suggest that all the goethite samples show bands at 636, 793 and 894 cm$^{-1}$ which are the characteristic bands of goethite and are due to OH bending vibrations. Similarly, the goethite samples show bands at 1383 and 833 cm$^{-1}$ for NO$_3^-$ moiety, which either disappear or present with reduced intensity after chromate adsorption. Thus, all the experimental findings suggest that chromate is adsorbed by all the solid samples through innersphere complexation at pH 5 and 7 by replacing OH$^-$, NO$_3^-$ and CO$_3^{2-}$ anions from the surfaces. However, at the lowest pH of 3, some outersphere complexes of chromate are also formed on the surface of solids.
1. INTRODUCTION

Oxide, oxyhydroxides and hydrated oxides of Fe are collectively termed as iron oxides. They are the most widespread metallic oxides in soils occurring in one or more of their mineral forms and aggregates in different climatic regions (Schwertmann and Taylor, 1989). These oxides are secondary minerals and are formed from the primary minerals through reactions of $\text{Fe}^{2+}$ ions released from Fe(II)-bearing silicates upon weathering (Oades, 1963; Schwertmann and Fechter, 1984; Schwertmann and Taylor, 1989). The changes in natural environments continuously modify the types of mineral phases of iron oxides, their composition and distribution in soils under the influence of different pedogenic factors.

The iron oxides content of soils usually ranges from 1 to 6 %, but in some cases it may be higher than 20%, especially in tropical soils (Jackson, 1964). $\text{FeO}_6$ or $\text{Fe(O,OH)}_6$ octahedron is the basic structural unit of all the iron oxides, in which each Fe atom is surrounded either by six O or by both O and OH ions (Stucki et al., 1985). The $\text{FeO}_6$ or $\text{Fe(O,OH)}_6$ octahedra in different iron oxides are linked in different ways, which give rise to the differences in their crystal structures (Wells, 1975). The naturally occurring iron oxide minerals are goethite ($\alpha$-$\text{FeOOH}$), hematite ($\alpha$-$\text{Fe}_2\text{O}_3$), lepidocrocite ($\gamma$-$\text{FeOOH}$), maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$), magnetite ($\text{Fe}_3\text{O}_4$) and ferrihydrite ($5\text{Fe}_2\text{O}_3.9\text{H}_2\text{O}$ or $\text{Fe}_5\text{HO}_8.4\text{H}_2\text{O}$) (Stucki et al., 1985; Schwertmann and Taylor, 1989).

Of all the iron oxides, goethite occurs in almost every soil type and climate region and is thought to be responsible for the yellowish-brown color of many soils and weathered materials (Schwertmann and Taylor, 1989). Its structure consists of double chains of $\text{FeO}_3(\text{OH})_3$ octahedra extending along the crystallographic Z-axis. These octahedra are bound to neighboring double chains by Fe-O-Fe and H bonds. Synthetic goethites have usually acicular or needle-like crystals, but this morphology is often less well developed in
soils. Fibrous goethite and grassy types of goethite aggregates have also been reported to occur in some soils (Nakai and Yoshinaga, 1980; Fordham et al., 1985; Cornell and Schwertmann, 1996). Natural goethite is, generally, imperfectly crystalline material, having large surface area and open channel structure, when it is formed under the influence of different pedogenic factors. The pre-existing metal cations like Al$^{3+}$, Mn$^{3+}$, Cr$^{3+}$, Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ etc. get incorporated into the crystal structure of goethite as a substitute for Fe$^{3+}$ ion (Burns and Burns, 1977; Ford et al., 1997). This impure form of goethite consisting of substituted metal cations of varying valances for Fe$^{3+}$ ion are referred to as metal ion doped goethite.

Adsorption is the accumulation of gas, vapor or liquid molecules at the interface between two immiscible phases and the surface properties such as surface chemical composition and structure, surface area, surface charge and surface geometry are the principal determinants of the reactivity of adsorbents. Goethite has a highly reactive surface due to complete hydroxylation which makes it an efficient sorbent and plays an important role in controlling the mobility of trace contaminants, plant nutrients, soil aggregation, soil classification and pedogenesis (Prasad, et al. 2006). Like other metal oxides, it also possesses pH dependent surface charges and thus, in an aqueous medium its surface may either be positively or negatively charged. At a certain pH value the magnitude of positive and negative charges on the surface become equal, as a result, the net charge on the surface is zero. This pH value is referred as the point of zero charge (pH$_{pzc}$/PZC) of the solid (McBride, 1989).

The hydroxylated and /or hydrated surface of goethite is highly reactive and is reported to further improve with the doping of metal ions in its crystals (Zhang et al. 2003; Lakshmipathiraj et al. 2006; Mohapatra et al. 2006). Therefore, the surface properties of metal-doped goethite become particularly important due to its widespread occurrence and abundance in natural environment. In the past decade a number of studies have been
performed to determine the surface properties of goethite (Krehula et al. 2006; Manceau, et al. 2000; Sudakar, et al. 2004; Huynh et al., 2002; Mohapatra et al. 2006). An overlook on the efforts of these researchers suggests that the incorporation of small amount of different metals could have a significant effect on the chemical and physical properties of goethite and hematite. However, most of the work reported in the literature is related to the effect of metals substitution on the crystallographic and physico-chemical properties of goethite. Only a few researchers have focused their attention on their potential use as adsorbents for the removal of heavy metals from aqueous solutions (Zhang et al. 2003; Lakshmipathiraj et al. 2006; Mohapatra et al. 2006; Wu et al. 2007; Liao et al. 2007). These studies revealed that incorporation of metal ions into goethite significantly increased its adsorption capacity for heavy metal contaminants. Further, in most of the studies involving metal-doped goethite as an adsorbent, attention is given only to arsenate and arsenite, the adsorption of Cr(VI) by Mn-substituted goethite was reported only recently by Wu et al. (2007) and it was observed that Mn-substituted goethite had greater adsorption capacity than pure goethite due to its greater surface area. Owing to the potential toxicity associated with Cr(VI), their results are important particularly from the environmental point of view.

Chromium is one of the known metal contaminants, released into the environment due to its extensive uses in industrial processes, such as the production of stainless steel, refractory products like brick and mortar, pigments manufacturing, treatment of metal surfaces and in leather tanning etc. (Bolan et al., 2003; Bayat, 2002). It exists in trivalent and hexavalent states in the environment. The trivalent Cr(III) occurs naturally and is an essential nutrient (Beliles, 1979), while the hexavalent chromium Cr(VI) which exists primarily in the form of chromate anions \((\text{Cr}_2\text{O}_7^{2-})\), \((\text{HCrO}_4^-)\) and \((\text{CrO}_4^{2-})\), is a strong oxidant that may cause kidney tubule necrosis and is also a known carcinogen (Beliles, 1979; Raji and Anirudhan, 1997). The recommended limit of Cr(VI) in potable water is
only 0.05 mg L\(^{-1}\) (Selvaraj et al., 2003). The industrial and mining effluents, however, contain much higher concentrations compared to the permissible limit which poses a serious threat to human as well as aquatic life.

On the other hand, in Pakistan the situation is rather worse. In a study carried out by Sirajuddin et al., (2007) on electrolytic recovery of chromium salts from tannery wastewaters of a local leather industry, it was reported that the average Cr(VI) contents of the wastewater were about 2550 mg L\(^{-1}\). The presence of Cr(VI) in the industrial effluents in such a large quantity is alarming and needs treatment and removal before discharging into the environment.

The potential toxicity associated with Cr(VI) has been globally acknowledged and various techniques have been used for its removal from the industrial wastewaters. These techniques include reduction and precipitation (Selvaraj et al., 2003), ion exchange (Neagu et al., 2003), solvent extraction (Patterson, 1978), electrochemical precipitation (Huang and Wu, 1975) and adsorption (Kongsricharoern and Polprasert, 1995). Among all these methods, adsorption has been proved to be the most promising technique due to its simplicity, greater efficiency, low cost and easy regeneration. As adsorption capacity and stability of the adsorbents are the main criteria for their selection; the study of adsorption properties of goethite could be of particular interest due to its natural abundance and stability. However, in spite of its stability in aquatic environment, its efficiency for the removal of heavy metal contaminants is rather poor. The doping of metal ions in goethite has been observed to improve significantly its adsorption capacity for the removal of various metal contaminants due to their presence in the solid matrix. The present study was, therefore, undertaken with the following aims and objectives;

- To study the affect of Pb\(^{2+}\), Cu\(^{2+}\) and Ni\(^{2+}\) ions doping on the physico-chemical properties of goethite as well as the adsorption behavior of goethite for chromate anions in aqueous medium.
• To study the physical, chemical and adsorption properties of amorphous copper and iron mixed oxides for chromate anions, formed by the coprecipitation method.

• To study the sorption of chromate on doped goethite as well as on amorphous phases of copper and iron mixed oxides and to compare them with the undoped goethite.

• To study the effects of concentration, pH and temperature on the sorption of chromate by metal(II) goethites and mixed oxides of copper and iron.

• To establish the mechanism of chromate anion sorption by the solid using various adsorption models, thermodynamic parameters and different spectroscopic techniques.
2. REVIEW OF LITERATURE

2.1 Occurrence of Goethite

Goethite (α-FeOOH) occurs abundantly in nature, as a constituent of terrestrial soils, sediments, oolitic iron ores and major weathering product of all type of rocks. The name “goethite” has been given after the name of German polymath Johann Wolfgang von Goethe. It was first described in 1806 for occurrences in the Mesabi iron ore district of Minnesota U.S.A. In younger sedimentary deposits, it is the predominant phase, giving the rocks a yellow color (Prasad, et al. 2006).

All the iron oxides, including goethite, are the weathering products, formed from the reactions of Fe^{2+} ion, released from Fe(II) silicates and sulfide minerals through protolysis and oxidation (Oades, 1963; Schwertmann and Fechter, 1984; Schwertmann and Taylor, 1989; Cornell and Schwertmann, 1996). Their formation and transformation afterwards depend upon the persisting pedo-environmental conditions, including temperature, moisture, pH, Eh, organic matter and ionic conditions.

Goethite is thermodynamically unstable at room temperature and is converted to hematite slowly with time. However, the conversion process is slow enough to exclude any substantial changes over the period of typical laboratory experiments (Kosmulski, et al. 2004). In nature, goethite is found most frequently associated with hematite in the tropical and subtropical regions (Segalen, 1971; Schwertmann et al., 1982). Generally, warmer and drier conditions favor the formation of hematite while cooler and moistened conditions favor the formation of goethite (Taylor and Graley., 1967; Kampf and Schwertmann., 1982)

Goethite can also be easily synthesized in the laboratory in the form of needle-like (aciccular) particles of submicrometer size with a very high specific surface area. Different preparation methods for synthetic goethite have been proposed and goethite samples with different specific surface areas and morphologies have been synthesized using different
experimental conditions. The main variables that have been reported to effect the surface areas and morphologies of goethite include the Fe precursor (nitrate, chloride, and sulfate etc.), the Fe:OH ratio or the final pH, the rate of their addition and the temperature (usually 40–90 °C) and time (a few hours to a few weeks) allowed for crystallization (Hiemstra and van Riemsdijk, 1996; Juang, and Wu, 2002; Trivedi, and Axe, 2001; Subrt et al., 2000).

The formation of goethite is reported to occur via deprotonation and hydrolysis of Fe(III) in dissolved state, which is then followed by nucleation and crystallization. The mechanism of goethite formation involving Fe(II) as a precursor, is even more complicated. A detailed discussion on the formation and transformation mechanism, and the effect of experimental conditions on the properties of goethite can be found in the elegant work of Cornell and Schwertmann, (1996).

2.2 Goethite as an Adsorbent

Goethite is considered to be an ideal adsorbent, due to its natural abundance in the earth’s surface (Sposito, 1984) and its well known surface chemistry (Machesky et al. 1989; Sposito, 1984). The surface reactivity and adsorption behavior of goethite have been extensively studied and its synthetic analogues have served as a reference for the development of many of the surface complexation models (Hiemstra and van Riemsdijk, 1996; Hiemstra, et al. 1989).

Adsorption is the accumulation of gas, vapor or liquid molecules on an interface. It is the most commonly employed technique for the removal of soluble metals and organic substances from aqueous phase and depends upon the surface properties of the adsorbent. Like other metal oxides goethite also possess pH dependent surface charges in aqueous medium which changes with pH according to the following reactions (Sun et al., 1999):

\[
= FeOH + H^+ \Leftrightarrow FeOH_2^+
\]  

(A)
In aqueous medium, the surface of goethite is, thus, either positively or negatively charged. At a certain pH value, the positive charge on the surface becomes equal to the negative charge, whereby the net charge on the surface is zero and this pH value is referred to as the point of zero charge (PZC) (McBride, 1989).

The pH_{pzc} of all the iron oxides including goethite depend upon their method of preparation and are found to be in the range of 6-10 for its different mineral phases (Parks and de Bruyn, 1962; Parks, 1965, 1967; Schwertmann and Fischer, 1982; Tipping and Cooke, 1982; Cornell and Schwertmann, 1996). This property is also influenced by the adsorbed cations and anions. As the adsorption of anions neutralizes the surface positive charge, therefore, their adsorption decreases the pH_{pzc} of iron oxides. On the other hand, adsorbed cations increases the pH_{pzc} of Fe oxides by increasing the surface positive charge (Parks, 1965).

Different methods, like potentiometric and mass titrations, salt addition (Kosmulski, 2009a, b), sum frequency vibrational spectroscopy (Yeganeh, et al., 1999) and batch technique (Balistrieri and Murray, 1981; Kinniburgh et al., 1975) etc. have been employed for measuring the pH_{pzc} of goethite. However, due to the limitations associated with these methods, different values of PZC have been reported for goethite. For example, goethite samples with pH_{pzc} values of about 6 to 9 have been frequently reported in the literature (Kosmulski, 2009a, Mohapatra et al. 2006; Lakshmipathiraj et al. 2006; Macesky et al., 1989; Boily et al. 2001). These differences are reported to be due to many reasons, the important one of which, however, is the presence of impurities like nitrate, carbonate, sulphate and chloride etc. in the solid matrix.

Metal ions doping also affects the pH_{pzc} value of goethite, as it leads to the formation of a mixed oxide of the doped metal and iron on the surface. In such a case, the pH_{pzc} is

\[ = FeOH \Leftrightarrow FeO^- + H^+ \text{ (B)} \]
reported to be the weighted average of the PZC values of the respective oxides (Stumm, 1992). Thus, certain metal cations, like Cu and Ni are reported to increase the $\text{pH}_{\text{pzc}}$ value of goethite (Mohapatra et al., 2006). While some other metal cations, like Mn$^{3+}$ is reported to decrease the PZC value of goethite (Sun et al., 1999).

### 2.2.1 Cation Adsorption

The hydroxylated and/or hydrated surface of goethite is highly reactive and plays a key role in the process of adsorption that occurs at goethite-water interface. Thus, the properties of goethite as an adsorbent for cations have been studied in a great detail. The cation adsorption is found to dependent upon different factors, like pH, temperature and background electrolyte concentration etc. Nature of the surface reactions has been determined by using different isotherms and surface complexation models. Various spectroscopic techniques, like XPS, FTIR, ATR, DR-FTIR and EXAFS etc. have been used to elucidate the reaction mechanism for metal ion adsorption by goethite (Trivedi et al., 2001; Abdel-Samad and Watson, 1998; Schwertmann and Taylor, 1989; Bargar et al. 1999). Further, an overview of the available literature, suggests that the goethite and metal cations interactions have been investigated in two different types of systems, i.e. single adsorbate system like goethite-Pb(II), goethite-Cu(II), goethite-Ni(II), goethite-Ca(II) etc. (Abdel-Samad and Watson, 1998; Grossl et al., 1994; Trivedi et al., 2001) and competitive adsorption systems (Christophi, and Axe 200; Balistreri, and Murray, 1982; Wang and Xing, 2004; Coughlin and Stone, 1995; Schwertmann and Taylor, 1989). Of these two systems competitive adsorption has been studied in relatively more detail due to its resemblance with the adsorption/desorption processes occurring in the natural environment.

Studies involving the single adsorbate systems reveal that transition metal cations have greater affinity for the surface of goethite. Most of the metal cations are reported to interact with the surface of goethite through the formation of different types of surface
complexes (Trivedi et al., 2001). The adsorption of Pb(II) onto the surface of goethite was studied by Abdel-Samad and Watson, (1998). It was observed that the Pb/Fe ratio at saturation was 0.93 with a high adsorption site density of 14.2 sites/nm$^2$. The high site density was attributed to the formation of polynuclear complex formation on the surface at high Pb(II) concentrations. Bargar et al., (1999) studied Pb(II)EDTA adsorption on goethite using ATR, DR-FTIR and EXAFS techniques. The uptake characteristics of Pb(II)EDTA$^{2-}$ by goethite suggested the formation of outer-sphere complexes or a hydrogen bonding mechanism in which carboxylate oxygens on the chelate were directly hydrogen bonded to protonated surface functional groups, displacing water of solvation from the PbEDTA(II)$^{2-}$.

The adsorption and desorption behavior of Zn(II) on water-goethite interface under various particle concentration and temperature were investigated by Xu et al., (2009). They observed that the effect of particle concentration was more pronounced at lower temperatures and the adsorption of Zn increased greatly with temperature. Similarly, the reversibility of Zn adsorption was also found to increase with temperature. They suggested from their observations that the process of Zn adsorption was chemisorption with $\Delta S = 195.71$ J/mol.K and $\Delta H = 34.07$ kJ/mol.

In natural system, however, multiple ions are present which are involved in a competition for the occupation of the active sites present on the surface of goethite. In such a system, adsorption of the competing ions is reported to depend upon both the nature of the metal ion and surface characteristics. From the adsorption edges and ionic strength effects Christophi, and Axe (2000) observed that copper, lead, and cadmium adsorbed specifically on goethite and the metal uptake capacity of the goethite increased with metal electronegativity as: Cu > Pb > Cd. Similarly, competitive adsorption of Cu, Pb, Zn, and Cd on goethite (α-FeOOH) from NaNO$_3$ solutions and from major seawater ions was carried out by Balistrieri, and Murray (1982). From their results they showed that, the
binding energies of Cu, Zn, and Cd with α-FeOOH for natural seawater concentrations could be estimated from the experimental data. Further, Cu, Pb, Zn, and Cd showed little or no competition for surface sites on goethite, and the presence of carbonate, phosphate, and silicate had little or no effect on the adsorption of Zn and Cd on goethite.

The effect of phosphate and its application time on Cd adsorption and desorption by goethite was investigated by Wang and Xing (2004), using a batch equilibration method. Their results demonstrated that the addition of phosphate into the system by the two sequences: pre-treating goethite at 40°C for one week and applying with Cd simultaneously, enhanced Cd adsorption, and facilitated the Cd release. Cadmium and its application time, on the other hand, had little impact on phosphate sorption by goethite. However, phosphate desorption kinetics was affected by Cd application time. Similarly, the effects of phthalic acid and chelidamic acid on Cu$^{2+}$ and Ca$^{2+}$ sorption were examined by Ali and Dzombak (1996) in goethite (α-FeOOH)/water system. Sorption of Cu$^{2+}$ was significantly enhanced at low pH values in the presence of the organic acids, particularly, chelidamic acid. Sorption of Ca$^{2+}$ was, however, found to remain unaffected by phthalic acid and decreased in the presence of chelidamic acid due to the formation of nonsorbing Ca$^{2+}$-chelidamic acid solution complexes. They suggested that enhanced sorption of Cu$^{2+}$ was the result of sorption of Cu$^{2+}$-organic acid complexes in a ligand-like manner.

From the sorption studies of Ni, Zn, and Ca onto the goethite surface Trivedi et al. (2001), observed that the adsorption affinity followed the order: Zn>Ni>Ca, according to the inverse of their hydrated radii multiplied by the number of water molecules in the primary solvation shell. Overall, metal affinities for goethite, with slight variations, are reported to follow the order: Cu>Pb>Zn>Cd>Co>Ni>Mn>Ca>Mg (McKenzie, 1980; Coughlin and Stone, 1995; Schwertmann and Taylor, 1989). Schwertmann and Taylor (1989) reported
this trend to be consistent with their electronegativities, while Christophi and Axe (2000) found it to be in agreement with the hydrated radii of the cations.

2.2.2 Anion Adsorption

Adsorption of various anions like arsenate, arsenite, silicate, tungstate, vanadate, antimonite, carbonate, phosphate, sulfate and chromate etc. on the surface of goethite has been studied extensively. However, in comparison to the cations, detailed studies involving the adsorption of anions are rather few. Further, to their more likelihood in natural environment, competitive adsorption studies in case of anions cover most of the reported literature. Moreover, a number of anions, like phosphate, sulphahte, arsenite, antimonite, vanadate and carbonate have been studied both individually and in competitive adsorption systems. Goethite has also been used as a model sorbent to examine the effect of pH, temperature, background electrolyte concentration, presence of other species in solution, etc. on the sorption process of anions.

2.2.2.1 Effect of pH

pH is an extremely important factor in any adsorption process and even a very small change in pH can have a pronounced effect on the extent of adsorption. Therefore, voluminous literature is available on the anion adsorption as a function of pH on the surface of goethite. Effect of pH on the adsorption of anions individually as well as in competitive adsorption systems has been evaluated in order to understand the mechanism of the interactions of anions with goethite in the natural environment. Phosphate and sulphahte adsorption onto goethite individually as well as in combination with each other, under different experimental conditions was investigated by Geelhoed et al., (1997). They observed that in systems having both the anions, the influence of phosphate on sulfate adsorption was much stronger than vice versa. Hence, it was concluded that phosphate has higher affinity than sulphate, for the surface of goethite. At total concentrations of $1 \times 10^{-4}$ M for both the anions, phosphate adsorption was observed to decrease slightly at pH
values below 4, whereas sulfate adsorption was much lower over the entire pH range below the PZC. Arsenite adsorption at different pH values and concentrations was studied by Kersten and Vlasova, (2009a). It was found that the adsorption of arsenite increases with pH, being highest at the pH of 9 and decreases at the higher pH values. It was also found that in the pH range 3 to 10 the amount of arsenite adsorbed by goethite surface remained close to almost 96% for a 10 µM arsenite initial solution; increased from 40% to 70% for a 50 µM initial solution, and from 30% to 45% for a 100 µM initial concentration, respectively. A maximum in arsenite adsorption near the pH<sub>PZC</sub> value, and some arsenite desorption at pH values above the pH<sub>PZC</sub> were also observed.

Peacock and Sherman, (2004) reported that adsorption of Vanadium (V) onto goethite in the pH range 6-9, under oxic (<i>PO</i><sub>2</sub> = 0.2 bar) conditions. The concentration dependence of adsorption reflected the formation of polynuclear complexes in solution when [V]<sub>total</sub> > 2.5 ppm. The over all adsorption was found to occur by the formation of inner-sphere surface complexes resulting from bidentate corner-sharing between doubly and singly protonated VO<sub>4</sub><sup>3-</sup> terahedra and FeO<sub>6</sub> polyhedra. Carbonate sorption onto goethite was studied by Villalobos and Leckie (2000), as a function of pH and ionic strength under both the closed (fixed total CO<sub>2</sub>) and open (fixed <i>P</i>CO<sub>2</sub>) conditions. They found that in closed systems maximum adsorption occurred between pH 6 and 7 (up to 0.5 mmol/m<sup>2</sup>, for 133 mM [CO<sub>2</sub>]<sub>tot</sub>), while in open systems around atmospheric a continuous increase in sorption with pH was observed. It was also reported that carbonate uptake enhanced the sorption of proton by direct adsorption or ligand exchange of the surface > OH groups. An average of 1.5 protons were sorbed per carbonate moiety adsorbed and remained approximately constant with pH for all the systems studied under investigation.

Phosphate and arsenate adsorption on goethite was investigated by Antelo et al., (2005) at different pH and electrolyte concentrations. They reported that phosphate adsorption was
more sensitive to changes in pH and ionic strength than that of arsenate. The combined effects of pH and ionic strength resulted in higher phosphate adsorption in acidic media at high ionic strength and result in its lower adsorption in basic media and low ionic strength. For phosphate the formation of three inner-sphere surface complexes: monodentate nonprotonated, bidentate nonprotonated, and bidentate protonated and for arsenate only two bidentate species were suggested. Luengo et al., (2007) also studied the effect of pH with other experimental condition like adsorbate concentrations, temperature and stirring rates on the adsorption of phosphate and arsenate by goethite. They observed that for both the oxyanions the adsorption rate increased by increasing the adsorbate concentration, decreasing the pH and increasing the temperature.

Molybdate adsorption onto goethite was reported by Xu, et al., (2006) with phosphate, sulfate, silicate, and tungstate as competing anions. They observed that tungstate and phosphate were the strongest competitors for molybdate, whereas little competitive effects were observed for the anions of silicate and sulfate. The charge distribution multi-site complexation (CDMUSIC) model was used to predict competitive adsorption between MoO$_4^{2-}$ and other anions (i.e., phosphate, sulfate, silicate and tungstate). The results of the model were in good agreement with the experimental adsorption behavior of molybdate over the pH range from 3.5 to 10. From the model predictions, it was suggested that molybdate and tungstate were retained mainly by the monodentate complexes formation on the surface of goethite.

2.2.2.2 Effect of Temperature

Temperature is also an important parameter affecting the rate and extent of sorption processes and it may change between winter and summer conditions by as much as 50 or 60°C in natural water and soil systems (Angove et al., 2006). Though, much is given in the literature about the effect of pH, some studies reporting the effect temperature on the
adsorption of anions onto the surface of goethite are also available in the literature. Kersten and Vlasova, (2009a), investigated the effect of temperature on the adsorption of arsenite by goethite. They carried out the adsorption of arsenite between 10 and 75°C using different arsenite concentrations and reported that the adsorption process was endothermic and arsenite formed two inner-sphere bidentate surface complexes on goethite. Application of the new constants with the aqueous speciation code VMINTEQ predicted that the As(III) concentration in the presence of goethite decreased by 10 times once the hydrothermal solution was cooled from 99 to 1°C. The adsorption of silicate onto the surface of goethite was also investigated by Kersten and Vlasova, (2009b) in the concentrations range between 10-100 μM using three different ionic strengths (0.01–0.1 M) and four different temperatures between 10-75 °C. The % Si adsorbed vs. pH curves showed an upward bend with a maximum at about a pH of 9. The pH-dependent Si adsorption at the goethite surface was modeled involving a single-site approach for both neutral and hydrolyzed silicate inner-sphere surface complexes. They concluded that both the species of silicate formed a binuclear bidentate surface complex. Adsorption of the silicate on the surface of goethite was reported to be exothermic for the dominating surface complex formed on the surface that became, therefore, weaker with increasing temperature.

Lazaridis and Charalambous, (2005) studied the sorption of trivalent and hexavalent chromium from binary aqueous solutions by composite alginate–goethite beads and reported that in the case of Cr(VI) the sorption capacity increased from 23.4 to 29.4mg/g while in the case of Cr(III) from 20.7 to 25.2 mg/g, when temperature was increased from 20 to 60°C. These findings suggested that the adsorption of trivalent and hexavalent chromium by composite alginate–goethite beads exhibited an endothermic behavior.
2.2.2.3 Thermodynamic Parameters

Thermodynamic data could be of particular interest in determining the nature and mechanism of the surface reactions. Therefore, thermodynamic parameters for the adsorption of anions onto the surface of goethite have been reported by a number of researchers. The values of different reported thermodynamic parameters are summarized in Table 1, with the respective references of work discussed here in.

Thermodynamic and kinetic data of Sb(III) adsorption was reported by Watkins et al., (2006) from single metal solutions onto goethite at pH 4 and 25°C. The sorption process was observed to be fast and the desorption occurred within 24 h of the reaction due to the oxidation of Sb(III) on the surface. At pH 4, the dominant antimonite species in solution were Sb(OH)₃ and HSbO₂ which both were adsorbed as inner sphere complexes on the positively charged goethite surface. They calculated the values of thermodynamic equilibrium constant \((K_{eq})\) and Gibb’s free energy \((\Delta G^\circ)\) and from the negative value of \(\Delta G^\circ\) the sorption process was suggested to be spontaneous.

Using the 1-pK charge distribution model in combination with a basic Stern layer model Kersten and Vlasova, (2009a,b), also studied the thermodynamic aspects of arsenite and silicate adsorption onto goethite and determined the Gibb’s free energy, enthalpy and entropy of the system. Thermodynamic parameters, shown in Table 1 were calculated from the following complexation reactions of arsenite;

\[
\begin{align*}
2\text{FeOH}^{0.5} + \text{As(OH)}_3 &\leftrightarrow (\text{FeO})_2\text{As(OH)}^{-1} + 2\text{H}_2\text{O} \\
2\text{FeOH}^{0.5} + \text{As(OH)}_2^- &\leftrightarrow (\text{FeO})_2\text{AsO}^2+ + 2\text{H}_2\text{O} \\
2\text{FeOH}^{0.5} + \text{Si(OH)}_4^0 &\leftrightarrow (\text{FeO})_2\text{Si(OH)}_{2}^{2+} + 2\text{H}_2\text{O} \\
2\text{FeOH}^{0.5} + \text{Si(OH)}_3^- &\leftrightarrow (\text{FeO})_2\text{SiO(OH)}^{2+} + 2\text{H}_2\text{O}
\end{align*}
\]
From the values of enthalpy and Gibb’s free energy, it was suggested that the adsorption process was spontaneous and exothermic.

Equilibrium sorption experiments for hexavalent and trivalent chromium ions from binary aqueous solutions by composite alginate–goethite beads were carried out by Lazaridis and Charalambous, (2005) at different temperatures and pH values. From the negative values of $\Delta G^o$ and positive values of $\Delta H^o$, $\Delta S^o$, they concluded that the adsorption process was spontaneous, endothermic and resulted in an increase in the randomness of the adsorbed species, respectively.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Temp. (ºC)</th>
<th>Reaction</th>
<th>$K_{eq}$ (L.g(^{-1}))</th>
<th>$\Delta G^o$ (kJ/mol)</th>
<th>$\Delta H^o$ (kJ/mol)</th>
<th>$\Delta S^o$ J.mol(^{-1})K(^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenite</td>
<td>10-75</td>
<td>C</td>
<td></td>
<td>-33.6</td>
<td>-26.0</td>
<td>26</td>
<td>Kersten and Vlasova, (2009a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>D</td>
<td></td>
<td>-32.1</td>
<td>-27.6</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Silicate</td>
<td>10-75</td>
<td>E</td>
<td></td>
<td>-30.1</td>
<td>-43.7</td>
<td>-46</td>
<td>Kersten and Vlasova, (2009b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F</td>
<td></td>
<td>-35.4</td>
<td>-21.7</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>chromate</td>
<td>20, 40, 60</td>
<td></td>
<td></td>
<td>-12.18</td>
<td>20.26</td>
<td>110.62</td>
<td>Lazaridis and Charalambous, (2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-14.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-16.61</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Table: 1  Thermodynamic parameters for anions adsorption on goethite.**

### 2.3 Chromate Adsorption

Anion adsorption in the literature has been given little attention as compared to cation adsorption. Among all the anions interaction of chromate with goethite achieved very little attention in spite of its environmental importance. Its adsorption onto the surface of goethite has been investigated by a few research workers, but the exact mechanism of the reaction is not clear as yet, due to the pH dependent complex chemistry of the chromate species (Li, 2004). Studies involving the interaction of chromate with goethite have mostly
addressed the effect of pH on the adsorption process and to the best of our knowledge, there is no study reporting the effect of temperature on the sorption of chromate by goethite.

Chromate adsorption onto the surface of goethite was studied by Abdel-Samad and Watson, (1997) as a function of pH and adsorbate concentration in 0.05 M NaNO₃. They reported that chromate adsorption increased with decreasing pH and eventually reached to a maximum at pH 6.5. From the XPS data, it was found that initially a small amount of chromium adsorbed in the +3 oxidation state via a redox reaction. However, majority of the chromium remained in the +6 oxidation state after adsorption. Lazaridis and Charalambous, (2005) observed an increase in the sorption capacity of goethite from 20.5 to 27.1 mg Cr/g of sorbent by decreasing the pH from 4 to 2. This was attributed to an increase in the surface positive charge of goethite with decreasing pH. They also attributed their results to the degree of protonation of the chromate molecule. Chromate, being a diprotic acid, would exhibit a much steeper adsorption edge as compared to a triprotic acid such as arsenate. This was because the adsorption of weak acid oxyanions was the strongest at the pH values near their acid dissociation constants (chromate pK₁ = 0.74) (McBride, 1994).

Karel and Fish, (1992) studied the adsorption of chromate and oxalate on goethite as a function of pH (4 – 11), ionic strength (0.01 – 0.5 M), adsorbate concentration (0.005 – 5 mM) and adsorbent dosage (0.08 –1.8 g /L). According to them, the adsorption of oxalate and chromate on α-FeOOH at low solution concentrations increased from 0 to 100 % with the decrease in pH and the pH edge for chromate was markedly steeper than for oxalate. Further, the fractional adsorption of both the anions became significant between pH 9 and pH 10, reflecting the pristine point of zero charge (PPZC) of the adsorbent. Moreover, the
absence of significant adsorption above the PPZC emphasized that a favorable electrostatic environment was necessary for the adsorption of these anions. Adsorption of chromate and oxalate by goethite was studied by Mesuere and Fish (1992a) for single-adsorbate systems as a function of pH, ionic strength and both adsorbate and adsorbent concentrations. Both the anions were found to exhibit Langmuir-type adsorption and increase in ionic strength was observed to decrease the adsorption of both the anions. However, oxalate was found to be more sensitive to the concentration of background electrolyte than chromate. Competitive adsorption of chromate and oxalate was also investigated by Mesuere and Fish, (1992b) as a function of adsorbate concentration. It was observed that at low pH near the surface saturation levels, oxalate effectively diminished the adsorption of chromate while chromate significantly inhibited oxalate adsorption over the entire pH range due to its high affinity for the surface of goethite. Diffuse layer and triple layer model simulations were found to be quantitatively accounted for binary solute adsorption as a function of pH, when the surface concentrations of both the adsorbates were high. In case, when the concentration of only one adsorbate was very low, the model predictions were very poor.

Due to the complex chemical nature of chromate, as mentioned earlier, both inner and outerspher complexes formation of chromate on goethite have been reported in the literature. Outer-sphere surface complexes are significantly affected by the increase or decrease in the ionic strength, thus yielding distinctly separated adsorption edges (Hayes and leckei 1987), while in case of inner-sphere mechanism such an observation cannot be made. Some of the published literature treated CrO$_4^{2-}$ as an outer-sphere complex (Ainsworth et al., 1989; Zachara et al. 1989), while in some other studies; innersphere complexation of chromate on goethite has been suggested. For example, van Geen et al. (1994) reported the formation of inner-spherically-formed CrO$_4^{2-}$ goethite surface complex in modeling the competition between CO$_3^{2-}$ and CrO$_4^{2-}$ ion. Similarly, Weerasooriya and
Tobschall, (2000) reported the inner-sphere surface complexation mechanism for chromate adsorption by goethite, which are shown in scheme 1.

Scheme 1: Complexes of CrO$_4^{2-}$ on goethite (A) monodentate binuclear (B) bidentate binuclear and (C) bidentate mononuclear.

Innersphere complexation is not the only mechanism for the adsorption of chromate by goethite, but some researchers, for example, Lazaridis and Charalambous, (2005), have also proposed an outersphere complexation mechanism, as shown in scheme 2.

Scheme 2: Outersphere chromate-goethite complex.

2.4 The Concept of Doping in Goethite

Goethite is poorly and imperfectly crystalline material having large surface area and open channel structure, when formed under earth’s surface conditions as a result of the hydrolytic reactions. These characteristics result in an unusual high capacity of goethite to incorporate, adsorb, and fix ions from the migrating solutions. Therefore, natural goethite usually contains a number of substituted cations of varying valences such as Al$^{3+}$, Mn$^{3+}$,
This isomorphous substitution of Fe$^{3+}$ in goethite by an other cation is termed as “doping”. The presence of cations other than Fe$^{3+}$ in goethite crystals are reported to significantly affect the physical and chemical properties of goethite (Stiers and Schwertmann, 1985).

Due to the changes occurring in the properties of goethite with the incorporation of the metal ions, many researchers have focused on the study of micro structural, physical and chemical properties of goethite in its synthetic analogues. Goethite, doped with manganese upto ~15mol%, was prepared by Stiers and Schwertmann, (1985), who reported that the originally added Mn$^{2+}$ is oxidized to Mn$^{3+}$ in goethite and resulted in the unit cell size to approach that of Groutite ($\alpha$-MnOOH). Ni-containing $\alpha$-FeOOH was prepared by Sudakar et al., (2004) by the oxidation of Fe(OH)$_2$·$x$H$_2$O precipitate in air at near neutral pH. They found goethite as a single phase structure by doping of Ni up to 5%. However, for more than 5% Ni doping, the formation of additional amorphous phases of Ni(OH)$_2$ or NiFe$_2$O$_4$ were suggested. Taylor and Schwertmann, (1978) found that Al$^{3+}$ ions inhibited the formation of lepidocrocite ($\gamma$-FeOOH) in favor of $\alpha$-FeOOH, when present in the solution used for the precipitation.

Unit cell parameters of synthetic doped goethite were investigated by Gerth, (1990) using Co$^{3+}$, Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ or Pb$^{4+}$ as dopents. He related the systematic changes of the unit-cell $b$-dimension with increasing substitution to the ionic radii of incorporated metals. The octahedra of the goethite structure became distorted along the crystallographic $a$-axis by incorporation of Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$. The distortion along $a$ in case of Zn- and Cd-goethite, was reported to be due to the smaller ionic size which both of these metals exhibited in the tetrahedral coordination. Thorium was found to be incorporated by non-structural incorporation while uranium was not incorporated at all. It was postulated that
the higher $a$-dimension in case of Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ was the result of structural defects and did not indicate the formation of a separate mineral phase.

Krehula et al., (2006) studied the influence of doped Zn on the precipitation of $\alpha$-FeOOH in highly alkaline media and reported that the samples precipitated in the presence of Zn$^{2+}$ ions showed the formation of solid solutions of $\alpha$-(Fe, Zn)OOH up to a concentration ratio $r = ([Zn]/([Zn] + [Fe]) = 0.0909$. ZnFe$_2$O$_4$ was additionally formed in the precipitate for $r = 0.1111$, whereas the three phases $\alpha$-FeOOH, $\alpha$-Fe$_2$O$_3$ and ZnFe$_2$O$_4$ were found for $r = 0.1304$. Dos Santos et al., (2001) studied the doping of gallium into goethite and found that gallium up to 10 mol% could be incorporated into $\alpha$-FeOOH. It was concluded that the incorporation of gallium resulted in the reduction of the crystallite size of the goethite.

The effects of Cu and Cr -dopant on the precipitation of $\alpha$-FeOOH and $\alpha$-Fe$_2$O$_3$ particles in highly alkaline media were investigated by Krehula and Music (2007, 2009). In the case of Cu-doping $\alpha$-(Fe, Cu)OOH solid solutions were found between $r = 0.0099$ and 0.0291, where ($r = [Cu]/([Cu] + [Fe])$) and a mixture of $\alpha$-(Fe, Cu)OOH and $\alpha$-(Fe, Cu)$_2$O$_3$ solid solutions formation resulted between $r = 0.0385$ and 0.0566. Whereas only $\alpha$-(Fe, Cu)$_2$O$_3$ solid solution was obtained in the limits of $r = 0.0698$ and 0.1666. Cr$^{3+}$ ions were found to be incorporated into the goethite crystals with $r$ values from 0 to 23.08 (where $r = 100[Cr]/([Cr] + [Fe])$). They also observed that an increase in the value of $r$ resulted in a decrease in the thickness of the lath-like $\alpha$-FeOOH particles. Schwertmann, (1984) prepared Al-goethites up to 10 mole% of Al and studied their dissolution in 6 M HCl at 24°C. The rate of the dissolution of synthetic Al-goethites was found to decrease markedly with increasing the extent of Al substitution. Most of the dissolution-time curves were S-shaped, suggesting an increase in surface area during the initial stages of dissolution. It was suggested that Al affected the dissolution rate of goethites indirectly by influencing the crystal growth rate which, in turn, affected both the crystal size and order.
Cerium-doped goethite (α-FeOOH) samples were prepared by Mohapatra et al., (2005) through aqueous precipitation route keeping the Ce(IV)/Fe(III) atomic ratio in the range of ~0.014 to ~0.07. From the XRD patterns, they showed that irrespective of the amount of metal doping, all the sample were well crystalline and showed only goethite as the crystalline phase. The cell parameter $a$ of goethite marginally decreased while $b$ and $c$ marginally increased as the Ce(IV)/Fe(III) atomic ratio increased to 0.035:1. However, further increase in this ratio showed much more increase in $b$ and $c$ cell parameters. On heating the samples to 673 K, goethite was completely transformed to nano-sized $\alpha$-Fe$_2$O$_3$ with the formation of small amount of cerium oxide. Further calcination to 1073K showed the formation of two distinct phases of CeO$_2$ and $\alpha$-Fe$_2$O$_3$. These findings suggested that goethite can accommodate a number of metal cations, when present during its synthesis and that these metal cations after incorporation changed its physical properties and chemical reactivity.

2.5 The Metal-doped Goethite as an Adsorbent

The adsorption capacity of adsorbents can be improved by the modification of its surface functional groups by the incorporation of foreign inorganic or organic compounds. For examples, modified activated carbons have been used as adsorbents to remove heavy metals for decades and are recognized as an attractive approach to enhance the heavy metals removal (Wu and Chong, 2003). The performance of a Zn-doped manganese oxide, as a regenerable sorbent was found to be very efficient in terms of low pre-breakthrough H$_2$S concentration in the outlet gas, high sorbent capacity and long durability (Alonso and Palacios, 2002). Similarly, in the presence of several bivalent cations such as Co$^{2+}$, Ni$^{2+}$ and Mg$^{2+}$, the percent adsorption of arsenite by ferrogeous manganese ore was also observed to increase (Chakravarty, et al., 2002). Therefore, a few researchers have also focused on the properties of doped goethite towards metal cations and anions.
The interaction of Mn-substituted goethite with arsenite (As(III)) was investigated by Sun et al., (1999) using both solution chemistry and X-ray adsorption near edge structure (XANES) spectroscopy. The reaction was found more sensitive to temperature than to pH. Their results indicated that the oxidation of As(III) was favored by Mn-substituted goethite. Zhang et al., (2003) studied the adsorption of As(V) on Ce-doped hydrous iron oxides and reported that in terms of adsorption pH range and adsorption capacity, the new adsorbent demonstrated a much better performance than activated alumina.

Mohapatra et al., (2006) reported that Cu, Ni or Co doped goethite was a better adsorbent for arsenic than the pure goethite itself. Liao et al., (2007) studied the structure and Mn$^{2+}$ adsorption properties of boron-doped goethite. It was reported that boron doping caused significant increase in the surface area of goethite and hence, increases the adsorption capacity of goethite for Mn$^{2+}$. Wu et al., (2007), reported adsorption of Cr (VI) on the Mn-substituted goethite and showed that chromate adsorption on goethite can be enhanced with Mn-doping due to increase in the specific surface area of goethite.

Though, there are some studies reporting the interaction of chromate with goethite in its pure state and to our knowledge only one study is present in the literature reporting the adsorption of chromate on Mn-doped goethite. However, the toxic nature of chromium and its extensive release into the soils necessitate detailed studies involving the interactions occurring at the metal ion doped-goethite surfaces. Further, the exploration of the adsorption of chromate by metal doped goethite could be of technological importance, and may be helpful in the processing and development of cheap and efficient sorbents. Therefore, the exploration of chromate and metal doped goethite interaction as a function of pH, temperature and adsorbate concentration is the main objective of the present investigation.
3. EXPERIMENTAL

3.1. Reagents and Solutions

All reagents used were of analytical grade. K$_2$CrO$_4$, HNO$_3$, KOH, NaOH, Fe(NO$_3$)$_3$·9H$_2$O, Pb(NO$_3$)$_2$, Ni(NO$_3$)$_2$·6H$_2$O and Cu(NO$_3$)$_2$·6H$_2$O were supplied by Merk and were used without further purification. All the solutions were prepared in doubly distilled water. Chromate solutions of different concentrations used in this study were prepared from a 1000ppm stock solution. pH adjustments were made by using 0.01 and 0.1M KOH or HNO$_3$ solutions. Standard buffers of pH 3, 7 and 11 were used for calibration of the pH meter.

3.2. Preparation of Pure and Metal (II) ion doped Iron Oxide Samples

The pure and metal (II) ion doped iron oxide samples used in this study were prepared according to the procedure reported in the literature (Schwertman and Cornell, 1991). For preparing pure iron oxide, 1M ferric nitrate solution was vigorously stirred at room temperature, to which 10M sodium hydroxide solution was added simultaneously under controlled conditions. The process was stopped as the final pH of the suspension reached between 11 and 12. The Pb$^{2+}$ and Ni$^{2+}$ doped samples were prepared by using the same procedure except that 2.5×10$^{-3}$ M Pb(NO$_3$)$_2$ solution and 1×10$^{-2}$ M Ni(NO$_3$). 6H$_2$O solutions were added to 1 M ferric nitrate solution. The Cu$^{2+}$ ion doped iron oxide samples were prepared by adding 1×10$^{-2}$, 5×10$^{-2}$ and 1×10$^{-1}$M Cu(NO$_3$)$_2$·6H$_2$O solutions to 1 M ferric nitrate solution, using the same procedure as described above. The suspensions thus obtained were aged for 48 hours at 343K and then washed thoroughly until the pH of the supernatant reached 7-8. The samples of goethite thus prepared were dried and were ground in an agate mortar, passed through a 70 mesh sieve and stored in a desiccator for further use.
3.3. **Chemical Analysis of the Iron Oxide Samples**

Chemical analysis of the iron oxide samples were carried out by dissolving a weighed amount of each sample in concentrated hydrochloric acid. The total iron, in the dissolved samples was determined volumetrically following the standard procedure reported in the literature (Vogel, 1962), while the amount of Pb, Ni and Cu in the solids was estimated by atomic absorption spectrophotometer (Perkin Elmer) model AAnalyst-800.

3.4. **Characterization**

Physical characterization of all the samples of iron oxide was carried out using the following techniques.

3.4.1 **Surface Area and Pore Volume**

BET surface area and pore volume of the iron oxide samples were estimated by N₂ adsorption method using Quantachrome NOVA 2200e surface area analyzer. Prior to the analysis, all the samples were degassed at 473 K for 2 h.

3.4.2 **Determination of pH of Point of Zero Charge (pHₚₑᵥ)**

The pH of point zero charge (pHₚₑᵥ) of all the solid samples was determined by the method of Kinniburgh et al., (1975). Suspensions of 0.2g of the solid sample in 40 ml of 0.1 M KNO₃ solutions were prepared in 50 ml volumetric flasks and the initial (pHi) of each suspension was adjusted to the desired value ranging from 3 to 11. The suspensions were then allowed to equilibrate for 24 hours in end-to-end shaker bath, labortechnic type LE-209 provided with hooks for 50ml flasks at constant temperature. After noting the final pH (pHf) value, the difference (ΔpH) between the initial and final pH values was calculated. The values of ΔpH were plotted against initial pH values which yielded the pHₚₑᵥ of the solid as the pH at which ΔpH=0.
3.4.3. **XRD**

X-Ray diffraction patterns of the air-dried finely powdered solid samples were recorded by using JEOL X-ray diffractometer, model JDX-7E with Mn filtered Cu-Kα radiations. The operating voltage and current were 20 kV and 20 mA respectively.

3.4.4. **FTIR**

FTIR spectra of the solids were recorded using SHIMADZU 8201PC, Fourier transform Infrared spectrophotometer. Samples for analysis were prepared by mixing KBr crystals with the sample in 2:1 ratio, which were dried at 378 K for 24 hours. The mixture was ground to fine powder again and was heated at 373 K for 12 hours, and then the mixture was subjected to IR observations. The analysis were performed at a resolution of about 4 cm⁻¹ and the No. of scans was about 10.

3.4.5. **TG-DTA**

Thermal analysis was performed on a simultaneous thermogravimetry/differential thermal analyzer (TG–DTA), Perkin Elmer, model 6300. The rate of heating was 10°C per minute and the samples were heated up to 600°C in nitrogen atmosphere.

3.4.6. **Transmission Electron Microscopy (TEM)**

The morphologies of the solids were examined by transmission electron microscopy (TEM, JEOL 100CX, Japan). The samples for TEM were prepared by taking 400 mg.L⁻¹ of the solid in deionized water and were sonicated for 30 minuets in order to get a good suspension. A very small drop from the suspension was taken on a copper TEM grid (Electron Microscopy Sciences, USA) and then placed in pitree dish for air-drying. The images were taken under high vacuum pressure at magnification of 5000 times.

3.4.7. **Scanning Electron Microscopy (SEM)**

For SEM micrographs, thin sections were prepared by putting fine grains of the solid sample in acetone and were kept for two minutes in an ultrasonic bath for the separation of
particles. Then a drop of this suspension was dried on a clean glass slide and finally the sample surface taken on the sample holder, was coated with a thin gold layer by a sputtering machine. The micrographs were obtained under different magnification power by using scanning electron microscope (SEM) JSM model 5910 [JEOL Co. Japan]. Operating voltage of the machine was 30 kV.

3.5. **Dissolution Studies**

Dissolution experiments of the solids were performed in the desired pH range, both in 0.1M KNO₃ and chromate solutions of different concentrations at 303K. Briefly, 40 ml of 0.1M KNO₃/chromate was taken in 50 ml conical flasks and 0.2g of the solid was added to each flask. The desired pH of each suspension was adjusted and the flasks were kept shaking for 24 hours at constant temperature in an end to end shaker bath. After recording the equilibrium pH, the suspensions were then filtered and the concentrations of Fe, Pb, Ni and Cu in the filtrate were determined by atomic absorption spectrophotometer.

3.6. **Adsorption Studies**

The adsorption isotherm experiments were carried out in an end-to-end shaker bath, Labortecnic type LE-209, provided with hooks for 50ml conical flasks. Chromate solutions of different concentrations, ranging from 0.25-2.01mmol/L, were prepared in doubly distilled water. All the chromate solutions contained 0.1M KNO₃ as a background electrolyte. 0.2g of the solid sample was added to each chromate solution taken in a 50ml Pyrex glass flask. Initial pH of each suspension was adjusted to the desired pH value, i.e. 3, 5 and 7. The flasks were then transferred into the shaker bath and were shaken for 24 hours at constant temperature.

The adsorption pH edge experiments for the samples of iron oxide prepared in the presence of Cu²⁺ ions, were performed in a similar manner, at 303K. These experiments involved a series of measurements as a function of pH (3–9), using a constant adsorbate
concentration, (0.6 and 1.8mmol/L chromate solutions) at a constant ionic strength of 0.1M KNO₃.

After noting the equilibrium pH, the suspensions were filtered out and the filtrate was analyzed for the equilibrium concentration of chromium by using atomic absorption spectrophotometer. The amount of metal ions sorbed was determined from the difference between the initial and the equilibrium concentration of the metal ions as:

\[ X = \frac{C_o - C_e}{m} V \]  

(1)

where \( C_o \) and \( C_e \) are the initial and equilibrium chromium(VI) concentration (mmol/L), \( X \) is the amount of chromate sorbed at equilibrium (mmol.g⁻¹), \( m \) is the mass of adsorbent (g) and \( V \) is the volume of the solution (L).
4. RESULTS AND DISCUSSION

Due to the involvement of different samples of goethite in the present study, the following nomenclature has been followed throughout the discussion to describe each sample;

- Pure goethite (α-FeOOH), (goethite sample devoid of any foreign element).
- Pb-doped goethite α (Fe, Pb)OOH, (goethite sample in which 0.38% Pb$^{2+}$ ion have been incorporated).
- Ni-doped goethite α (Fe, Ni)OOH, (goethite sample in which 0.25% Ni$^{2+}$ ion have been incorporated).
- Cu-doped goethite α (Fe, Cu)OOH, (goethite sample in which 0.32% Cu$^{2+}$ ion have been incorporated).

The results obtained for each metal(II) ion doped goethite sample, have been separately sectioned in this chapter and thoroughly compared with pure goethite in a bid to remain consistent with the theme of the present investigation. All the solid samples have been characterized for surface area, pH of point of zero charge (pH$_{pzc}$), XRD, TG-DTA, TEM/SEM and FTIR analysis. Chromate adsorption studies on all the goethite samples mentioned above have been carried out at pH 3, 5 and 7 in the temperature range 303-323K. Mechanism of the chromate-goethite interaction for each sample has been proposed in the light of available data. Moreover, due to the promising behavior of the Cu-doped goethite for the removal of chromate, the adsorption properties of two more samples of iron oxide with 6.27 and 11.31% Cu$^{2+}$ ions were also investigated. The results obtained for these samples are compiled in the last section of this chapter and compared with 0.32% Cu-doped goethite, following the nomenclature given below;

- HMO-I, represent, Cu-doped goethite, as described earlier.
- HMO-II, represents the iron oxide sample containing 6.27% Cu$^{2+}$ ion
- HMO-III, represents the iron oxide sample containing 11.31% Cu$^{2+}$ ion
These samples are also characterized for surface area, pH of point of zero charge (pH\textsubscript{pzc}), XRD, SEM and FTIR analyses. Langmuir parameters and isosteric heat of adsorption have also been determined for the highest copper containing sample from the adsorption data.
4.1 Characteristics and Chromate Adsorption Properties of Pb-Doped Goethite

4.1.1 Characterization

4.1.1.1 Surface Area
Surface area, pore volume and chemical analysis of both the samples of goethite are given in Table 1, which show that Pb-doping has a pronounced effect on the surface area and pore volume of goethite. The surface area of goethite increases from 34.69 to 77.80 m² g⁻¹, while the pore volume decreases to about one half. The changes in surface area and pore volume of Pb-doped goethite seem to be due to the larger ionic radius of Pb²⁺ ion as compared to Fe³⁺ ion. The difference in ionic radii of Pb²⁺ [r(Pb²⁺)=1.19Å] and Fe³⁺ [r(Fe³⁺)=0.645Å] is about 0.545Å, which causes local contraction/expansion in the edges and corners of the crystal planes of goethite, hence affecting its surface area and pore volume (Mohapatra et al., 2006; Manceau et al., 2000).

4.1.1.2 pH of Point of Zero Charge (pH_{pzc})
The increase in surface area of goethite with Pb-doping results in an enhanced capacity of the Pb-doped goethite to adsorb H⁺/OH⁻ ions. This behavior of the Pb-doped goethite leads to the larger ΔpH values for this sample of goethite and are evident from Figure 4.1. The Figure also shows that pH of point of zero charge (pH_{pzc}) of goethite increases from 7.25 to 7.45 with Pb²⁺ ions doping. The increase in the pH_{pzc} of the Pb-doped goethite, is due to the presence of Pb²⁺ ions in the form of Pb(OH)₂ on the surface of the solid. This mineral phase is expected to exist due to the experimental conditions imposed on the solid during preparation, given in section 2.2 and pH-dependent speciation of the Pb²⁺ ions (Ozverdi and Erdem, 2006). It has been reported that the point of zero charge of a composite oxide is approximately the weighted average of the values of its components (Stumm, 1992). The pH_{pzc} of the Pb-doped goethite i.e. 7.45, is lower than the weighted average of the pH_{pzc} values of Pb(OH)₂ and α-FeOOH which are 11 (Liu and Liu, 2003) and 7.25 respectively.
The weighted average of their $\text{pH}_{\text{pzc}}$ values comes out to be 9.225. Zhang et al., (2003) found similar results for Ce-doped goethite. The increase in $\text{pH}_{\text{pzc}}$ of goethite with metal ions doping is in agreement with the studies reported by Mohapatra et al., (2006).
Figure: 4.1  pH of point of zero charge for pure and Pb-doped goethite in 0.1M KNO₃ at 303K.
4.1.1.3 TG-DTA

Figure 4.2 (A) and (B), show TG-DTA curves for pure and Pb-doped goethite respectively, which show that both the solids lose a small weight at about 50°C. In the temperature range 250-300°C, the weight loss for pure goethite is about 8.92% and for Pb-doped goethite, it is 7.99%. The resultant endothermic peaks can also be noted from the Figure. These weight losses are due to the removal of physically adsorbed water and hydroxyl groups (Chitrakar et al., 2006) and the topotactic transformation of goethite to hematite, according to reaction (4.1), suggested by Diamandescu et al., (1997).

\[
2 \alpha - FeOOH \rightarrow \alpha - Fe_2O_3 + H_2O \quad (4.1)
\]

The doped sample, however, shows a third weight loss of about 9.22% with an endothermic peak above 540°C, which seems to be due to the removal of water molecules from Pb(OH)$_2$, present in goethite crystals forming PbO, as well as due to the decomposition of $NO_3^-$ ions present in the solid (Han et al., 2006).

4.1.1.4 XRD Patterns

XRD patterns of goethite, given in Figure 4.3 (A) and (B) show that both the solids are crystalline. The Figure also shows that both the solids have characteristic d-spacing values of 4.20, 2.69 and 2.45, which are characteristic d-spacing values of goethite (Abdel-Samad and Watson, 1998) with a slight change in the values particularly the d-spacing value of 4.20 occur at 4.18 for Pb-doped sample. These changes seem to be due to the changes in the unit cell parameters caused by the different ionic radii of Fe(III) and Pb(II) as reported by Campo et al., (2008) for Mn and Co-doped goethites. They related the changes in unit cell parameters of goethite to the differences in ionic radii of these ions to Fe$^{3+}$ ion.
Figure: 4.2  TG-DTA curves for (A) pure and (B) Pb-doped goethite.
Figure: 4.3  XRD pattern of (A) pure goethite and (B) Pb-doped goethite.
4.1.1.5 Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)

Figure 4.4 (A) and (B) show TEM images of pure and Pb-doped goethite respectively, which indicate that both the samples of goethite have typical needle like crystals of goethite. The length and width of the crystals calculated are $0.917 \pm 0.18$ and $0.190 \pm 0.014 \mu m$ for pure and $1.719 \pm 0.576$ and $0.3439 \pm 0.105 \mu m$ for Pb-doped goethite, which suggests that the doping of $Pb^{2+}$ ions results in an increase in the particle size of goethite. Effect on the size of goethite particles by metal ions incorporation has been reported by many researchers (Campo et al., 2008; Nakayama et al., 2005; Chitrakar et al., 2006). Traces of an amorphous phase along with the crystals of goethite can also be noted in the TEM image (B) of Pb-doped goethite. Further the particles of goethite seem to have sub-grain boundaries, which results in the rough texture of goethite crystals evident from the micrograph. Similar effects on goethite crystals were reported by Nakayam et al. (2005) for Ti-doping in goethite. The surface roughness is more evident in the Scanning Electron Micrograph, of the Pb-doped goethite shown in Figure 4.4 (C). These observations suggest that a discrete phase of $Pb(OH)_2$ exists within the solid phase as was suggested earlier, from the thermo gravimetric behavior of the solid.

4.1.1.6 FTIR Studies

Figure 4.5 (A) and (B), show FTIR spectra for pure and Pb-doped goethite sample, with a band at $636 \text{ cm}^{-1}$, which is due to Fe-O symmetric stretching (Lakshmipathiraj et al; 2006), and two bands at 793 and $894 \text{ cm}^{-1}$, which are characteristic bands of goethite, arising due to OH bending vibrations (Cambier, 1986). The band at $1383 \text{ cm}^{-1}$, in both the samples of goethite, which is broader and intense in Pb-doped goethite, was assigned to $NO_3^-$ group (Hu et al., 2007). The $NO_3^-$ ions may have entered the solid as the nitrate salts were used for the preparation of goethite. The peak at $833 \text{ cm}^{-1}$ in Pb-doped is also due to nitrate ions (Brooker and Irish, 1968), present as an impurity in the solid. The characteristic IR bands of goethite as
can be noted in pure goethite have been shifted slightly in Pb-doped goethite and such a shift in peak position with metal ions doping in goethite has already been reported in the literature (Krehula et al., 2005).
Figure: 4.4 TEM images (A) pure goethite, (B) Pb-doped goethite and (C) Scanning Electron Micrograph of Pb-doped goethite.
Figure: 4.5 FTIR spectra (A) pure goethite and (B) Pb-doped goethite.
4.1.2 Dissolution Studies

Dissolution behavior of both pure and Pb-doped goethite, in 0.1M KNO₃, and 303K is given in Figure 4.6 (A), which shows that under the given experimental conditions Pb-doped goethite dissolve more readily than pure goethite and that the release of iron decreases with increasing pH. The release of Pb from Pb-doped goethite is also given in Figure 4.6 (b), which exhibit the same trend with the increasing pH, as observed in Figure 4.6 (A). Further, it can be noted from these Figures that the amount of iron released from Pb-doped goethite is almost twice the amount of iron released from pure goethite. This dissolution behavior of Pb-doped goethite seems to be due to the enhanced dissolution of the Pb(OH)₂ phase in the solid matrix. It has been reported that lead oxide dissolve extensively in acidic condition (Hsu et al. 2006).

From Figure 4.6 (C) it can be noted that increasing chromate concentration from 0.25 to 1.25 mmol/L, Pb release decreases and reaches a constant value at 1.25 mmol/L of chromate concentration. This behavior of the Pb-doped goethite is consistent with the observations of Eick et al. (1999), who reported that oxyanions inhibit the dissolution of goethite. However as shown in Figure 4.7 (A, B, C), dissolution of Pb-doped goethite increases with an increase in the concentration KNO₃, which is in contrast to the behavior of pure goethite, though the trend with increasing pH is the same as stated earlier. These results suggest that NO₃⁻ anion inhibits iron leaching from the solid matrix. However, the enhanced dissolution of Pb-doped goethite is due to the presence of Pb ions in the solid, which are improperly aligned in its crystals and hence are leached easily by increasing the ionic strength. The improper alignment of Fe and Pb ions in the doped goethite occur due to the larger ionic radius of Pb²⁺ ion as compared to Fe³⁺ ion. This explanation is consistent with our XRD and FTIR results, and also with the literature (Campo et al., 2008) which suggest that the presence of Pb in the solid affects the geometry of the crystals of goethite.
Figure: 4.6 (A) Iron release as a function of pH from pure and Pb-doped goethite in 0.1MKNO₃ at 303K, (B) Pb release from Pb-doped goethite in 0.1MKNO₃ and (C) Pb release from Pb-doped goethite as a function of chromate concentration at 303K.
Figure: 4.7 (A) and (B) Iron release as a function of pH from pure and Pb-doped goethite respectively, in different concentrations of MKNO₃ at 303K, (C) Pb release from Pb-doped goethite in different concentrations of MKNO₃ at 303K.
4.1.3 Adsorption Studies

4.1.3.1 Effect of pH

Effect of pH on the adsorption of chromate on both the samples of goethite is shown in Figures 4.8 (A) and (B), which clearly shows that chromate adsorption decreases with increasing pH. This behavior is due to the decrease in surface charge of goethite with increasing pH, according to the following equilibria (Dixit and Hering, 2003);

\[ FeOH + H^+ \rightarrow FeOH_2^+ \]  \hspace{1cm} (4.2)

\[ FeOH \rightarrow FeO^- + H^+ \]  \hspace{1cm} (4.3)

The surface Pb(OH)\(_2\) will exist in the protonated form as PbOH\(_2^+\), below its point of zero charge i.e. pH-11. Therefore, the presence of PbOH\(_2^+\) groups on the surface with the increase in surface area would lead to an increase in the uptake of negatively charged chromate species HCrO\(_4^-\); the dominant species between pH-2 and 7 (Erdem et al., 2004). The increase in the adsorption capacity of goethite is evident from Figure 4.9, which shows that Pb-doped goethite adsorb about 20% more chromate than pure goethite under similar experimental conditions except at pH 7, where the margin in the adsorption capacity is lesser.

Dissolution behavior of the solid suggests that the release of Pb from Pb-doped solid is almost similar in both 0.1M KNO\(_3\) and in 1.02 mmol.L\(^{-1}\) chromate solution i.e. about 4-5 x 10\(^{-3}\) mmol.L\(^{-1}\) at pH-3 and 303K, which suggest that lead chromate (PbCrO\(_4\)) is not formed in the system. As far as the release of iron is concerned, it was not found in the solution phase at any concentration of chromate, from both the samples of goethite. The disappearance of iron from the solution phase suggests that the dissolved iron is precipitated on the surface of the solid according to the mechanism proposed by Hongshao and Stanforth (2001) for the precipitation of Fe\(^{3+}\) on the solid surface due to the dissolution of goethite.

In order to predict the nature of interaction between goethite surface and chromate anions, the changes in equilibrium pH of the suspension were monitored and are given in Table 4.3, which shows that the equilibrium pH values of the suspension have decreased at pH-3, and
increased at pH 5 and 7. The increase in the equilibrium pH shows that at pH 5 and 7 chromate is adsorbed on goethite surface through, innersphere surface complexation as:

\[ FeOH + HCrO_4^- \rightarrow FeHCrO_4 + OH^- \]  (4.4)

Similarly, on the Pb(OH)_2 surface as:

\[ PbOH + HCrO_4^- \rightarrow PbHCrO_4 + OH^- \]  (4.5)

Similar innersphere complexation has been proposed for the chromate adsorption by many authors (Weerasorriya and Tobschal, 2000; Eick et al., 1999). As far as, the anomalous decrease in equilibrium pH at pH 3 is concerned, it seems to be due to the hydrolytic dissolution of the solid, releasing Fe^{3+} and Pb^{2+} ions into the aqueous solution and also due to the difference in chromate adsorption mechanism at this pH. As, following the mechanism, suggested for pH 5 and 7, one would expect a greater increase in the equilibrium pH at pH 3, where the maximum sorption of chromate is observed on both pure and Pb-doped goethite. However, unexpectedly the equilibrium pH decreases instead of being increased, therefore, the dominant mechanism responsible for chromate uptake at this pH is outersphere rather than innersphere complextaion. Because, at this pH the surface of the solid is highly protonated according to reaction (4.2). Therefore, the adsorption process on both the samples of goethite at pH 3 can be represented by the following equations.

\[ FeOH_2^+ + HCrO_4^- \rightarrow FeOH_2^+ - HCrO_4^- \]  (4.6)

\[ PbOH_2^+ + HCrO_4^- \rightarrow PbOH_2^+ - HCrO_4^- \]  (4.7)

Hu et al. (2005) proposed the same mechanism for chromate adsorption on γ-Fe_2O_3 at pH 2.5 and 8.

### 4.1.3.2 Effect of Temperature

Effect of temperature on the adsorption of chromate on pure and Pb-doped goethite is shown in Figure 4.10 (A) and (B) respectively, where it can be noted that in case of pure goethite adsorption increases with increasing temperature while in case of Pb-doped goethite,
adsorption decreases with increasing temperature. In case of pure goethite the % adsorption of chromate increases from 62.8% to 72.2%, while in case of Pb-doped goethite it decreases from 82.3% to 75.1% by increasing the temperature from 303 to 323K. It shows that the process of adsorption is endothermic in case of pure goethite and exothermic in case of Pb-doped goethite. Both endothermic and exothermic adsorption of oxyanions had been reported in the literature (Erdem et al., 2004; Mallick et al., 2006).
Figure: 4.8  Adsorption isotherms for (A) pure goethite and (B) Pb-doped goethite at 303K (suspension density 5mg/ml).
Figure: 4.9  Comparison of chromate sorption capacity (%) of pure and Pb-doped goethite as a function of pH, using 0.78 mmol/L chromate solution at 303K (Suspension density; 5mg/ml).
Figure: 4.10 Effect of temperature on the adsorption of chromate on (A) pure goethite and (B) Pb-doped goethite at pH-3 (suspension density 5mg/ml).
4.1.4 Adsorption Isotherm

Langmuir Isotherm was applied to the adsorption data in the following form;

\[
\frac{C_e}{X} = \frac{1}{(K_bX_m)} + \frac{C_e}{X_m}
\]  

(4.8)

where \(C_e\) is the equilibrium \(\text{Cr(VI)}\) concentration (mmol.L\(^{-1}\)), \(X\) is the amount of \(\text{Cr(VI)}\) sorbed at equilibrium (mmol.g\(^{-1}\)), \(K_b\) the adsorption equilibrium constant (L.mmol\(^{-1}\)) that is related to the apparent energy of adsorption; \(X_m\) is the maximum monolayer capacity of the adsorbent (mmol.g\(^{-1}\)). The model was fitted to the data for both pure and Pb-doped samples at temperatures 303, 313 and 323K and pH 3, 5 and 7. The equation was found applicable to the data over the whole concentration range considered in the present investigation.

The values of Langmuir constants \(X_m\) and \(K_b\) calculated from the plots of \(Ce/X\) vs \(C_e\), Figure 4.11 (A) and (B), are given in Table 4.2, which suggest that Pb-doped goethite has larger values of both the Langmuir parameters. Larger values of \(X_m\) denote greater monolayer adsorption capacity of Pb-doped goethite. Similarly, greater values of \(K_b\), the binding energy constant, show that chromate is more firmly bound to the surface of Pb-doped goethite. These observations are in agreement with the results depicted in Figure 4.9. Similar conclusions were made by Mohapatra et al. (2006) for increase in the values of Langmuir constants, while investigating the adsorption of Arsenate on metal doped goethite.

4.1.5 Isosteric Heat of Adsorption

Isosteric heats for the adsorption of chromate on both the samples of goethite were determined from Clausius Clapyron Equation, by plotting \(\ln Ce(r)\) vs \(\frac{1}{T}\), according to the relation;

\[
\ln Ce(r) = \frac{\Delta H}{RT} + \text{Constant}
\]  

(4.9)

where \(C_e\) is the equilibrium concentration of chromate at constant coverage, \(R\) is the molar gas constant (8.314JK\(^{-1}\)mol\(^{-1}\)), \(T\) the absolute temperature and \(\Delta H\) is the isosteric heat of
adsorption. The values of $\Delta H$ were calculated from the plots of plots of $\ln C_e$ vs $1/T$ which are shown in Figure 4.12 (A) and (B). As expected the values of $\Delta H$, in Table 4.4, are positive for pure goethite while negative for Pb-doped goethite, which, as suggested earlier, show that the process of adsorption is endothermic in case of pure goethite and exothermic in case of Pb-doped goethite. The Table also shows that the heat of adsorption decreases with increasing surface coverage in both the cases, which is due to the heterogeneity of the surface (Choudhary et al., 1988). Similar decrease in isosteric heat of sorption with increasing surface coverage was reported by Sharma (2001) for chromate adsorption on Wollastonite. Further, the exothermic nature the chromate sorption is in agreement with the greater capacity of the Pb-doped goethite for the $\text{H}^+$/OH$^-$ ions as depicted in Figure 4.1. The sorption of $\text{H}^+$ ions on the surface of goethite is exothermic to the extent of -58 KJmol$^{-1}$ as reported by Angove et al. (1999). The increase in sorption of chromate will also lead to an increase in the sorption of $\text{H}^+$, resulting in more negative values of $\Delta H$. This explanation also agrees with the outersphere complexation of the chromate anions on Pb-doped goethite at pH 3. It has also been noted by Eick et al. (1999) that with the increase in chromate surface coverage the outersphere complexes are replaced by innersphere complexes. Thus the decrease in the $\Delta H$ values on goethite observed here also points towards the above mentioned changes in the mechanism of the process, while the negative values observed for the Pb-doped goethite are due to the predomination of the outersphere complexes on this adsorbent.

4.1.6 FTIR Studies

FTIR spectra for chromate sorbed Pb-doped goethite at pH 3, 5 and 7 at 303K are shown in Figure 4.13 (A), (B), and (C). The spectra show all the characteristic bands of goethite, already discussed in section 4.1.1.6, along with certain apparent changes after treatment with chromate solutions, which can be summarized as follows;

1. By comparing the spectra (A), (B), and (C) in Figure 4.13 with the spectrum of Pb-doped goethite in Figure 4.5 (B), it can be noted that the strong absorption band of
nitrate at 1383 cm\(^{-1}\), in the spectrum of Pb-doped goethite in Figure 4.5 (B), decreases in intensity after treatment with chromate solutions, due to their exchange with \(\text{HCrO}_4^-\) from aqueous solution. This is also supported by the observation that the band at 833 cm\(^{-1}\), which is also due to nitrate, disappears completely after treatment with chromate solutions.

2. The intensity of the bands in the Pb-goethite between 700-900 cm\(^{-1}\), intensifies after treatment with chromate solution. This increase in the intensity of the IR bands is probably due to the overlapping of the absorption bands of \(\text{HCrO}_4^-\) and Fe-O and OH groups of goethite, as the splitting of Cr-O stretching mode in the 770-1000 cm\(^{-1}\) range are reported to be due to the coordinated CrO\(_4\) group (Repka et al;1998).

3. A smaller band at 958 cm\(^{-1}\) is evident at all the pH values of 3, 5 and 7, which matches well with the \(\nu_1\) vibration band of free CrO\(_4^{2-}\) anion in solution, suggesting that some of the chromate species are adsorbed by the solid surface through the electrostatic forces of attraction (Hu et al., 2007). This type of chromate adsorption is referred to as, outersphere surface complexation. Similar results were found by Prasanna et al. (2006) for Layered double hydroxide and by us (Mustafa et al., 2008) for \(\beta\)-MnO\(_2\). As such, the presence of three different sorption mechanisms can be proposed for the chromate uptake by Pb-doped goethite i.e. (i) outer surface complexation at low pH value of 3 (ii) innersphere complexation at high pH values of 5 and 7 (iii) ion exchange with \(\text{NO}_3^-\) ions from the solid.
Figure: 4.11 Langmuir plots for (A) pure goethite and (B) Pb-doped goethite at 303K (suspension density 5mg/ml).
Figure: 4.12 Plots of Clausius clapeyron equation at pH-3 for (A) pure and (B) Pb-doped goethite.
Figure: 4.13 FTIR spectra for Pb-doped goethite (A) pH 3, (B) pH 5, (C) pH 7, after treatment with chromate solutions.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²g⁻¹)</th>
<th>Pore Volume (cm³g⁻¹)</th>
<th>Fe (%)</th>
<th>Pb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Goethite</td>
<td>34.69</td>
<td>0.02</td>
<td>62.4</td>
<td>-</td>
</tr>
<tr>
<td>Pb-doped Goethite</td>
<td>77.80</td>
<td>0.01</td>
<td>57.6</td>
<td>0.384</td>
</tr>
</tbody>
</table>

**Table: 4.1** Surface characteristics and chemical composition of pure and Pb-doped goethite.

<table>
<thead>
<tr>
<th>pH</th>
<th>Pure Goethite</th>
<th>Pb-doped Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xₘ</td>
<td>Kₜ</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>14.52</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>16.14</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>7.62</td>
</tr>
</tbody>
</table>

**Table: 4.2** Langmuir parameters Xₘ (mmolg⁻¹) and Kₜ (Lmmol⁻¹) for pure and Pb-doped goethite.
Table: 4.3  Changes in equilibrium pH of pure and Pb-doped goethite suspensions in various concentrations of chromate at 303K.

<table>
<thead>
<tr>
<th>Initial Chromate Concentration ($\times 10^1$ mmol.L$^{-1}$)</th>
<th>Pure goethite</th>
<th>Pb-doped goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 3  pH 5  pH 7</td>
<td>pH 3  pH 5  pH 7</td>
</tr>
<tr>
<td>$pH_i$ $pH_f$ $pH_i$ $pH_f$ $pH_i$ $pH_f$ $pH_i$ $pH_f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.45  2.98  2.92  5.02  5.52  6.97  7.21  2.99  2.92  5.00  5.39  7.00  7.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.72  3.04  2.87  5.04  5.64  6.98  7.13  3.01  2.93  4.97  5.34  7.00  7.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.36  2.95  2.91  5.01  5.77  6.98  7.10  3.01  2.95  5.00  5.37  6.97  7.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.16  3.01  2.88  4.98  5.43  7.00  7.22  3.02  2.94  4.98  5.40  7.00  7.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.06 2.96  2.88  5.02  5.45  6.97  7.24  3.01  2.91  4.99  5.34  6.99  7.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.02 2.96  2.87  4.99  5.40  7.00  7.25  2.99  2.91  4.96  5.33  7.00  7.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.26 2.98  2.89  5.03  5.35  6.97  7.20  3.02  2.92  4.97  5.21  6.97  7.31</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: 4.4  Changes in $\Delta\bar{H}$ values (KJmol$^{-1}$) with increasing surface coverage ‘X’ (mmol.g$^{-1}$) for chromate adsorption on pure and Pb-doped goethite at pH 3 and 303K.

<table>
<thead>
<tr>
<th>Pure goethite</th>
<th>Pb-doped goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td>X  $\Delta\bar{H}$</td>
<td>X  $\Delta\bar{H}$</td>
</tr>
<tr>
<td>0.04  51.15</td>
<td>0.06 -16.47</td>
</tr>
<tr>
<td>0.06  28.20</td>
<td>0.08 -16.51</td>
</tr>
<tr>
<td>0.08  10.65</td>
<td>0.10 -28.12</td>
</tr>
<tr>
<td>0.1  13.67</td>
<td>0.12 -34.44</td>
</tr>
<tr>
<td>0.12  3.13</td>
<td>0.14 -41.88</td>
</tr>
</tbody>
</table>
4.2 Effect of Ni$^{2+}$ ion doping

4.2.1 Characterization

4.2.1.1 Surface Area

Surface characteristics and chemical composition of both the samples of goethite are given in Table 4.5, which shows that surface area has been increased from 34.69 to 125.99 m$^2$ g$^{-1}$, while pore volume from 0.02 to 0.06 cm$^3$ g$^{-1}$ by doping Ni$^{2+}$ ions in goethite matrix. The increase in surface area with Ni$^{2+}$ ions doping has already been reported elsewhere (Mohapatra et al., 2006), while the increase in the pore volume of goethite with Ni$^{2+}$ ions doping may be due to the distortion in the goethite structure by the presence of Ni$^{2+}$ as reported for Mn-doped goethite (Alvarez et al., 2006).

4.2.1.2 pH of Point of Zero Charge ($pH_{pzc}$)

The pH of point of zero charge ($pH_{pzc}$) of both the samples of goethite was investigated in 0.1M KNO$_3$ at 303K, and is given in Figure 4.14. It can be seen from this Figure that $pH_{pzc}$ of goethite increases from 7.25 to 7.5 with Ni$^{2+}$ ions doping, which agrees well with earlier studies (Mohapatra et al., 2006). The Figure also shows a significant increase in the $\Delta pH$ values for Ni-doped goethite, both above and below the $pH_{pzc}$. This shows an increase in the sorption capacity for $H^+$/OH$^-$ ions by the Ni-doped solid, probably on account of the NiO/Ni(OH)$_2$ formation on the surface (Hernandez et al., 2005).
Figure: 4.14 Point of Zero Charge for pure and Ni-doped goethite in 0.1M KNO₃ at 303K.
4.2.1.3 XRD Patterns

XRD pattern of both pure and Ni-doped goethite are shown in Figure 4.15 (A) and (B), which suggest that both the solids are crystalline in nature, with d-spacing values of 4.206, 2.69 and 2.45, which are characteristic of goethite and are in good agreement with the literature (Abdel-Samad and Watson, 1998). However, by comparing both the spectra, it can be noted that the peaks at 3.04 in pure goethite disappears in Ni-doped goethite, which may be due to the changes in the lattice parameters of goethite crystals arising from the Ni$^{2+}$ ions doping.

4.2.1.4 TG-DTA

Figure 4.16 (A) and (B) shows thermogravimetric (TG) and differential thermal analysis (DTA) for both samples of goethite, which shows a total weight loss of 13.338% for pure goethite and 18.595% for Ni-doped goethite. It can be seen from the Figure that along with a smaller weight losses at about 50°C, there is about 8.923% weight loss for pure and 8.125% weight loss for Ni-doped goethite with an endothermic peak at about 280°C, which is due to the loss of physically adsorbed water molecules (Chitrakar et al., 2006), topotactic transformation of goethite to hematite according to reaction (4.1) and conversion of Ni(OH)$_2$ to NiO as:

$$\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O} \quad (4.10)$$

Similar conclusions were made by Liang et al. (2004) for the conversion of Ni(OH)$_2$ to NiO. However, in case of Ni-doped goethite a third weight loss (about 3.279%) with an endothermic peak at 540°C is observed. This weight loss is probably due to the loss of water molecules changing the surface Ni(OH)$_2$ into NiO. It has been reported by Li et al. (2008) that heating of Ni(OH)$_2$ beyond 282°C causes the removal of all the intercalated water molecules from the interslab spaces in Ni(OH)$_2$ sheet, which results in the formation of NiO.

4.2.1.5 Transmission Electron Microscopy (TEM)

Figure 4.17 shows TEM images of pure and Ni-doped goethite, which shows that both the goethite samples have rod shaped particles with calculated lengths of 0.917± 0.18 um and
0.995 ±0.17um for pure and Ni-doped goethite respectively. The width of the pure goethite particles was 0.190 ± 0.014 um, while that of Ni-doped goethite was 0.213 ±0.045um, which suggests a slight increase in the particle size in case of Ni-doped goethite, that may be due to the local deformation of the crystal structure of goethite with Ni doping. However, it can be inferred from the images that up to the degree of Ni-doping in this study (0.25%), the basic structure of goethite has not been significantly affected as reported by Krehula et al. (2005).

4.2.1.6 FTIR Studies

Figure 4.18 shows the FT-IR spectra for both pure and Ni-doped goethite. The bands at 636, 792 and 894 cm\(^{-1}\) in the spectrum of pure goethite are the important diagnostic bands of goethite, of which the bands at 792 and 894 cm\(^{-1}\) are due to OH bending vibration (Cambier, 1986), while the band at 636 cm\(^{-1}\) is due to Fe-O symmetric stretching (Lakshmipathiraj et al., 2006). The band at 1382 cm\(^{-1}\), in both the spectra, is due to \(\text{NO}_3^\rightarrow\) group, as was also assigned to the presence of \(\text{NO}_3^\rightarrow\) by Hu et al. (2007). A smaller peak at 829 cm\(^{-1}\) can also be seen in the spectrum of Ni-doped goethite, which is also due to nitrate ions (Brooker and Irish, 1968), present as an impurity in the solid. In case of Ni-doped goethite the bands at 636 and 894 cm\(^{-1}\) in pure goethite show a slight shift in peak positions and are noted at 637 and 891 cm\(^{-1}\). Such a shift in peak position with the incorporation of Ni\(^{2+}\) ions in goethite has already been reported in literature (Krehula et al., 2005).
Figure: 4.15 XRD Pattern of (A) Pure and (B) Ni-doped goethite.
Figure: 4.16 TG-DTA curves of (A) pure and (B) Ni-doped goethite.
Figure: 4.17 TEM images of (A) pure and (B) Ni-doped goethite.
Figure: 4.18 FTIR spectra of pure and Ni-doped goethite.
4.2.2 Dissolution Studies

Figure 4.19(A) shows Fe release from both pure and Ni-doped goethite in 0.1MKNO$_3$, which suggest that Ni-doped goethite, dissolves more readily than pure goethite at pH 3, while at the rest of the pHs Ni-doped goethite is more stable than pure goethite. The enhanced dissolution of Ni-doped goethite at pH 3 is due to the fact that at pH< 3.5 Ni exist either in the cationic form i.e. Ni$^{2+}$ or as NiOH$^+$ (Hernandez et al., 2005; Palmer et al., 2004), which provide positive sites for NO$_3^-$ anions to interact with the surface, thereby destabilizing the goethite crystal and hence promoting dissolution. The effect of NO$_3^-$ anion on the release of iron from pure and Ni-doped goethite was also studied in 0.01, 0.1 and 0.5M KNO$_3$ and the results are given in Figure 4.20 (A), (B) and (C), which shows that dissolution of Ni-doped goethite increases with increasing concentration of KNO$_3$, while the reverse is true for pure goethite. This mechanism is further supported by the maximum release of Ni from Ni-doped goethite matrix at pH-3 as shown in Figure 4.19(B). It also shows that Ni release drastically decreases with increasing pH and at pH 6 Ni concentration in the solution phase reaches below the level of instrument detection limits.

While it has been reported in the literature that oxyanions like chromate and arsenate, inhibit dissolution of goethite (Eick et al., 1999), here it was found true only in case of pure goethite. Figure 4.19(C), shows Ni-release as a function of chromate concentrations, where it can be seen that the concentration of dissolved Ni remains almost constant in the presence of different concentration of chromate and decreases with increasing pH. Fe was not detected in the solution phase in anyone of the goethite samples. The absence of Fe in the solution in both the samples may be due to the adsorption of Fe on chromate, according to the mechanism proposed by Hongshao and Stanforth, (2001) for the adsorption of phosphate and arsenate on the surface of goethite. Due to its trivalency, iron is preferentially adsorbed to form surface precipitate, leaving behind Ni in the solution phase, though the contribution of
Ni in the surface precipitation cannot be excluded, but the subject is beyond the scope of the present studies.
Figure 4.19 (A) Iron release as a function of pH from pure and Ni-doped goethite in 0.1MKNO₃ at 303K, (B) Ni release from Ni-doped goethite in 0.1MKNO₃ and (C) Ni release from Ni-doped goethite as a function of chromate concentration at 303K.
**Figure: 4.20** (A) and (B) Iron release as a function of pH from pure and Ni-doped goethite respectively, in different concentrations of MKNO₃ at 303K, (C) Ni release from Ni-doped goethite in different concentrations of MKNO₃ at 303K.
4.2.3 Adsorption Studies

4.2.3.1 Effect of pH

Figure 4.21 (A) and (B) show isotherms for chromate anion sorption on pure and Ni-doped goethite. It is evident from these Figures that adsorption of chromate by both the samples of goethite is favored at lower pH and maximum adsorption occurs at pH 3. The maximum adsorption of chromate at lower pH is due to the increase in the magnitude of positive charge on goethite surface with decreasing pH according to reaction 4.2.

At pH-3 the goethite surface is protonated therefore, favoring the adsorption of the negatively charged chromate species HCrO$_4^-$ which is the dominant species between pH 2 and 7 (Erdem et al., 2004). The increase in %adsorption of goethite with Ni doping is shown in Figure 4.22, where it can be seen that in case of pure goethite the % adsorption increases from 36.2% at pH 7 to 61.4% at pH 3, while for Ni-doped goethite the same decrease in pH results in the increase in %adsorption from 45.2 to 82.92%. The increase in % adsorption of goethite with Ni doping may be due to the greater surface area and pore volume of this sample of goethite. Another reason for the increase may be the formation of Ni(OH)$_2$ on the surface as discussed in section 3.1. The % adsorption in both the cases was calculated at 323K for 1.02 mmol.L$^{-1}$ of chromate solution.

4.2.3.2 Effect of Temperature

Figures 4.23 (A) and (B) show the effect of temperature, on the adsorption of chromate on pure and Ni-doped goethite respectively, which suggests that adsorption increases with increase in temperature. Both the samples of goethite shows a marked increase in % adsorption, where in case of pure goethite the % adsorption increases from 47.2 to 61.4%, at pH 3 using 1.02 mmol. L$^{-1}$ Cr (VI), when the temperature is increased from 303 to 323K. Under similar conditions the % adsorption of Ni-doped goethite increases from 61.3 to 82.92%. This behavior suggests the endothermic nature of the adsorption process (Sharma,
2001) in both the cases and also an improvement in the % adsorption of chromate removal by goethite with Ni^{2+} doping.
Figure: 4.21 Sorption Isotherms for chromate (A) pure goethite and (B) Ni-doped goethite at 303K (Suspension density; 5mg/ml).
Figure: 4.22 Increase in % chromate uptake capacity of goethite with Ni doping from 1.02 mmol.L⁻¹ chromate solution at 303K (Suspension density; 5mg/ml).
Figure: 4.23 Amount of chromate sorbed at pH 3 by (A) pure goethite and (B) Ni-doped goethite at different temperatures (Suspension density; 5mg/ml).
4.2.4 Adsorption Isotherm

Langmuir adsorption isotherm, given in equation 4.8 was fitted to the data for both pure and Ni-doped samples at temperature 303, 313 and 323K and pH 3, 5 and 7. By plotting Ce vs Ce/X, straight lines with $R^2$ values between 0.97 to 0.99 were obtained for both the samples of goethite, which shows that this form of Langmuir isotherm is well fitted to the experimental data over the whole concentration range studied.

Figure 4.24(A) and (B) shows Langmuir plots for both the samples of goethite at 303K and pH 3, 5 and 7. The values of langmuir constants $X_m$ and $K_b$ are given in Table 4.6, which were calculated from the linear plots of Ce vs Ce/X for both the samples of goethite. It is evident from the Table that the values of $X_m$ are higher for Ni-doped goethite as compare to pure goethite at all the pH value being investigated, suggesting that Ni-doped goethite has greater capacity to adsorb chromate, which is in agreement with the adsorption behavior of both the samples of goethite given in Figure 4.21. Similar increase in the adsorption of arsenate was reported by Mohapatra et al. (2006) with Ni doping in goethite.

4.2.5 Isosteric Heat of Adsorption

Isosteric heat of sorption (the amount of heat evolved at constant coverage) was calculated by using Clausius Clapyron Equation, given in equation 4.9. The plots of $\ln Ce(r) \frac{1}{T}$ are straight line as shown in Figure 4.25 (A) and (B). The values of $\Delta H$ calculated form these plots at pH 3 and 5 and are given in Table 4.7, where it can be seen that $\Delta H$ values are positive for the adsorption process on both the samples of goethite. As already suggested the positive values of $\Delta H$ show the adsorption process to be endothermic in nature (Mustafa et al., 2002).

It is also noteworthy that the heat of adsorption decreases with increasing surface coverage in case of pure goethite, while the reverse is true for Ni-doped goethite. The decrease in isosteric heat of sorption with increasing surface coverage in case of pure goethite may be attributed to the heterogeneity of the surface (Choudhary et al., 1988). However in case of Ni-
doped goethite, the increase in the values of $\Delta H$ with increase in surface coverage seems to be due to the increased sorbate-sorbate interaction on the surface. According to Srivastava et al. (2007) the decrease in the isosteric heat of adsorption with surface coverage is the result of reduced adsorbate-adsorbent interaction, while the reverse is on account of increased adsorbate-adsorbate interactions. Probably along with the sorbate-sorbate interactions, the increase in the values of $\Delta H$ points towards the fact that the NiO/Ni(OH)$_2$ formed on the surface of goethite is also involved in the sorption of chromate. Moreover, comparatively higher values of $\Delta H$ at almost all surface coverages for Ni-doped goethite suggests that chromate adsorbs more strongly to the doped sample, as was suggested by Guo et al. (2006) for the higher heat of adsorption of carbon disulfide on carbon.

4.2.6 FTIR Studies

Figure 4.26 (A) (B) and (C) shows FTIR spectra of Ni-doped goethite after treatment with 1.02 mmol/L chromate solution at pH 3, 5 and 7 and 303K. The spectra show some interesting changes after treatment with chromate solutions. Comparing these spectra with the spectrum of Ni-doped goethite in Figure 4.18, it can be noted that the peak for nitrate anion at 1382 cm$^{-1}$ decreases in intensity, while the peak at 829 cm$^{-1}$ disappears completely. The band at 1540 cm$^{-1}$ evident in the spectrum of Ni-doped goethite in Figure 4.18, which is due to the split $\nu_3$ modes of surface carbonates (Karmakar et al., 2004), disappears as well, after treatment of the solid with chromate. These observations suggest that the surface nitrate and carbonate anions are replaced by chromate. Similarly the bands at 792 and 891 cm$^{-1}$ are shifted to lower wavenumbers i.e. 791 and 890 cm$^{-1}$ and are marginally intensified with chromate treatment. This increase in the intensity of the IR bands is probably due to the overlapping of the absorption bands of CrO$_4^{2-}$ and OH groups of goethite, as the splitting of Cr-O stretching mode in the 770-1000 cm$^{-1}$ range are reported to be due to the coordinated CrO$_4$ group (Repka et al., 1998), showing that surface OH groups are also exchanged with chromate from the solution. A new band appears at 958 cm$^{-1}$, which may be assigned to
and it agrees well with the ν1 vibration band of free \(CrO_4^{2-}\) anion in solution (Kantcheva and Vakkasoglu, 2004), suggesting that some of the chromate species is adsorbed to the solid surface through weak electrostatic forces of attraction by forming an outer surface complex (Hu et al. 2007). As in outer sphere complex at the water mineral interface, generally, the oxyanions retains their hydration shell forming no direct chemical bonding with surface (Petit et al., 1995).

### 4.2.7 Mechanism of the Surface Reaction

The equilibrium pH changes given in Table 4.8 shows that there is decrease in the equilibrium pH at pH 3, while the equilibrium pH increases at pH 5 and 7, suggesting that the mechanism of chromate uptake by the solids, at pH-3, is different from the mechanism at pH 5 and 7. At pH 3 the dominant mechanism may be described as electrostatic interaction between chromate anions (\(HCrO_4^-\)) and the positively charged goethite surface forming an outer surface complex as:

\[
FeOH_2^+ + HCrO_4^- \rightarrow FeOH_2^+ - HCrO_4^- \quad (4.11)
\]

and in case Ni-doped goethite:

\[
NiOH_2^+ + HCrO_4^- \rightarrow NiOH_2^+ - HCrO_4^- \quad (4.12)
\]

while the drop in pH may be due to the enhanced dissolution of both the solids at pH 3, discussed earlier in section 4.2.2. However at pH-5 and 7 the mechanism seems to change from simple electrostatic interactions to ion exchange resulting in the release of OH⁻ ions into the solution phase and hence increasing the pH as:

\[
FeOH + HCrO_4^- \rightarrow FeHCrO_4 + OH^- \quad (4.13)
\]

\[
NiOH + HCrO_4^- \rightarrow NHhiCrO_4 + OH^- \quad (4.14)
\]

Similar conclusions were made by Hu et al. (2005) for the adsorption of chromate on Maghemite nanoparticles at pH 2.5 and 8. Keeping in view the FTIR results and equilibrium pH changes the presence of three different sorption mechanisms can be proposed for the
chromate uptake by both the samples of goethite i.e. (i) outer surface complexation at low pH value of 3 (ii) innersphere complexation at high pH values of 5 and 7 (iii) ion exchange with $NO_3^-$ ions from the solid.
Figure: 4.24 Langmuir plots for adsorption of chromate by (A) pure goethite and (B) Ni-doped goethite (Suspension density; 5mg/ml).
Figure: 4.25 Plot of Clausius clapeyron equation at pH3 for (A) pure and (B) Ni-doped goethite.
Figure: 4.26 FTIR spectra for chromate treated Ni-doped goethite at (A) pH 3 (B) pH 5 (C) pH 7.
### Table: 4.5

Surface characteristics and chemical composition of pure and Ni-doped goethite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Goethite</td>
<td>34.69</td>
<td>0.02</td>
<td>62.4</td>
<td>-</td>
</tr>
<tr>
<td>Ni-doped Goethite</td>
<td>125.99</td>
<td>0.06</td>
<td>60.2</td>
<td>0.25</td>
</tr>
</tbody>
</table>

### Table: 4.6

Langmuir constants $X_m$ (mmol.g⁻¹) and $K_b$ (L.mmol⁻¹) for pure and Ni-doped goethite at 303K.

<table>
<thead>
<tr>
<th>pH</th>
<th>Pure Goethite</th>
<th>Ni-doped Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$X_m$</td>
<td>$K_b$</td>
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<tr>
<td>3</td>
<td>0.14</td>
<td>11.44</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>17.82</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>2.96</td>
</tr>
</tbody>
</table>
### Table: 4.7 Changes in $\Delta H$ values (KJmol$^{-1}$) with increasing surface coverage ‘X’ (mmol.g$^{-1}$) for chromate adsorption on pure and Ni-doped goethite at 303K.

<table>
<thead>
<tr>
<th>X</th>
<th>$\Delta H$</th>
<th>X</th>
<th>$\Delta H$</th>
<th>X</th>
<th>$\Delta H$</th>
<th>X</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>51.15</td>
<td>0.02</td>
<td>35.38</td>
<td>0.025</td>
<td>1.69</td>
<td>0.02</td>
<td>9.06</td>
</tr>
<tr>
<td>0.06</td>
<td>28.20</td>
<td>0.04</td>
<td>38.76</td>
<td>0.05</td>
<td>9.06</td>
<td>0.04</td>
<td>20.91</td>
</tr>
<tr>
<td>0.08</td>
<td>10.65</td>
<td>0.06</td>
<td>31.34</td>
<td>0.075</td>
<td>28.33</td>
<td>0.06</td>
<td>34.38</td>
</tr>
<tr>
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</tr>
<tr>
<td>0.12</td>
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<td>38.43</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
<td>65.71</td>
<td>0.12</td>
<td>45.66</td>
</tr>
</tbody>
</table>

### Table: 4.8 Changes in equilibrium pH of pure and Ni-doped goethite suspensions in various concentrations of chromate at 303K.

<table>
<thead>
<tr>
<th>Initial chroma Concentration (mmol.L$^{-1}$)</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$pH_i$</td>
<td>$pH_f$</td>
<td>$pH_i$</td>
<td>$pH_f$</td>
<td>$pH_i$</td>
<td>$pH_f$</td>
</tr>
<tr>
<td>0.22</td>
<td>2.98</td>
<td>2.92</td>
<td>5.02</td>
<td>5.52</td>
<td>6.97</td>
<td>7.21</td>
</tr>
<tr>
<td>0.50</td>
<td>3.04</td>
<td>2.87</td>
<td>5.04</td>
<td>5.64</td>
<td>6.98</td>
<td>7.13</td>
</tr>
<tr>
<td>0.78</td>
<td>2.95</td>
<td>2.91</td>
<td>5.01</td>
<td>5.77</td>
<td>6.98</td>
<td>7.10</td>
</tr>
<tr>
<td>1.02</td>
<td>3.01</td>
<td>2.88</td>
<td>4.98</td>
<td>5.43</td>
<td>7.00</td>
<td>7.22</td>
</tr>
<tr>
<td>1.17</td>
<td>2.96</td>
<td>2.88</td>
<td>5.02</td>
<td>5.45</td>
<td>6.97</td>
<td>7.24</td>
</tr>
<tr>
<td>1.43</td>
<td>2.96</td>
<td>2.87</td>
<td>4.99</td>
<td>5.40</td>
<td>7.20</td>
<td>7.25</td>
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<td>1.55</td>
<td>2.98</td>
<td>2.89</td>
<td>5.03</td>
<td>5.35</td>
<td>6.97</td>
<td>7.20</td>
</tr>
</tbody>
</table>
4.3 Effect of Cu\(^{2+}\) ion doping

4.3.1 Characterization

4.3.1.1 Surface Area

Table 4.9 shows surface area and pore volume of pure and Cu-doped goethite, where it can be seen that copper doping in goethite increases its surface area from 34.7 to 126.5 m\(^2\)g\(^{-1}\) and pore volume from 0.02 to 0.06 cm\(^3\)g\(^{-1}\). The increase in the surface area and pore volume of goethite with copper doping seems to be due to the difference in the ionic radii of Fe\(^{3+}\) and Cu\(^{2+}\). The ionic radii of Cu (0.73 Å) is \(~14\%\) greater than Fe (0.645 Å). Consequently its incorporation into the α-FeOOH framework results in a displacement of higher shells relative to those in goethite. It has been reported that the local variations in interatomic distances are compensated, to a greater extent, by the so called relaxation and compliance effects to retain the basic framework of goethite crystals (Manceau et al., 2000). However, the presence of the foreign element still has an effect on the unit cell parameters of goethite crystals (Zhang et al., 2003), which results in the increased porosity and surface area of the Cu-doped solid. Similar effect of copper doping on the properties of goethite was reported by Mohapatra et al. (2006).

4.3.1.2 pH of Point of Zero Charge (pH\(_{pzc}\))

Figure 4.27, shows changes in ΔpH as a function of initial pH (pHi), for both the samples of goethite and the pH at which ΔpH = 0 is the point of zero charge (pH\(_{pzc}\)) of goethite. The pH\(_{pzc}\) of both the samples of goethite, as shown in Figure 4.27, is about 7.5, which suggest that copper doping has no effect on this property of goethite and this is in agreement with the observations of Mohapatra et al. (2006). However, the Figure shows relatively larger ΔpH values for Cu-doped goethite as compare to pure goethite, which may be due to the greater capacity of Cu-doped goethite to adsorb H\(^+\)/OH\(^-\).
Figure: 4.27  Point of Zero Charge for pure and Cu-doped goethite in 0.1M KNO$_3$ at 303K.
4.3.1.3 XRD Patterns

XRD patterns of pure and Cu-doped goethite are given in Figure 4.28 (A) and (B), which shows that both the solids are crystalline in nature and consisting of all the characteristic d-spacing values reported for goethite (Abdel-Samad, and Watson, 1998). However, by close inspection of both the spectra it can be noted that some of the d-spacing values like 3.04, 2.08 and 1.92, observed in the spectrum of pure goethite, disappears in the spectrum of Cu-doped goethite. The difference in the d-spacing values of pure and Cu-doped goethite may be due to the changes in the lattice parameters of goethite, as suggested earlier, due to the presence of Cu$^{2+}$ ions in the solid.

4.3.1.4 TG-DTA

Figure 4.29 (A) and (B) shows TG-DTA curves for pure Cu-doped goethite samples respectively, where it can be noted that the total weight loss for pure goethite is about 13.34% and for Cu-doped goethite it is about 14.82%. Between 200-300°C there is about 8.92% weight loss for pure goethite and 8.82% for Cu-doped goethite with broad endothermic peaks. These weight losses are due to the loss of physically adsorbed water molecules as well as the transformation of goethite to hematite (reaction 4.1) and Cu(OH)$_2$ to CuO according to the following reaction (Chitrakar et al. 2006; Diamandescu et al., 1997; Singh et al., 2009);

$$Cu(OH)_2 \rightarrow CuO + H_2O$$  \hspace{1cm} (4.15)

However, the TG-DTA curve for Cu-doped goethite shows a second weight loss of about 1.44%, with a smaller endothermic peak. This weight loss seems to be due to the conversion of interlayer Cu(OH)$_2$ to CuO, losing water molecules as well as the decomposition of NO$_3^-$ anions present in the solid structure (Han et al., 2006).

4.3.1.5 Transmission Electron micrographs (TEM)

Figure 4.30 shows TEM micrographs for pure (A) and Cu-doped (B) goethite, where it can be noted that both the samples of goethite have needle like crystals of goethite. The dimensions of pure and Cu-doped goethite are in the order of $0.190 \times 0.917\mu$m and $0.197 \times 0.896\mu$m.
respectively, which shows that the doping of Cu has no effect on the morphology of goethite crystals. The little variations, particularly, the slight decrease in the length of Cu-doped goethite particles is due to the presence of Cu$^{2+}$ in its crystals and it is in agreement with earlier studies (Alvarez et al., 2006; Campo et al., 2008; Nakayama et al., 2005).

4.3.1.6 FTIR Analysis

FTIR spectra for pure (A) and Cu-doped (B) goethite are shown in Figure 4.31, where it can be seen that the spectrum of pure goethite shows the characteristic bands of goethite at 636, 792 and 894 cm$^{-1}$. The band at 636 cm$^{-1}$ is due to Fe-O symmetric stretching (Lakshmipathiraj et al.; 2006) and the bands at 793 and 894 cm$^{-1}$ are due to OH bending vibrations (Cambier, 1986). The band at 1382 cm$^{-1}$, in both the spectra was assigned to NO$_3^-$ group (Hu et al., 2007), while the IR band at 3105 cm$^{-1}$ is due to stretching mode of free surface hydroxyl group (Sudakar et al. 2002). The bands at 636, 792 cm$^{-1}$ in the spectrum of pure goethite can be noted at relatively lower wavenumber i.e. 632 and 790 cm$^{-1}$ in the spectrum of Cu-doped goethite, which is reported to be the result of the metal ions present in the crystals of goethite (Krehula and Music 2007).
Figure: 4.28 XRD Pattern of (A) Pure and (B) Cu-doped goethite.
Figure: 4.29  TG-DTA curves of (A) pure and (B) Cu-doped goethite.
Figure 4.30  TEM images (A) pure goethite and (B) Cu-doped goethite.
Figure: 4.31 FTIR spectra of (A) pure (B) Cu-doped and (C) chromate solution treated Cu-doped goethite.
4.3.2 Dissolution Studies

Figure 4.32 (A) shows iron release as function of pH for pure and Cu-doped goethite. It can be seen from the Figure that Cu-doped goethite dissolve more readily than pure goethite at pH-3, while above this pH value, it is more stable than pure goethite. The enhanced dissolution of the doped goethite at pH 3 may be due to the enhanced leachability of Cu as compared to iron in acidic conditions (Jandov et al., 2000). This behavior of Cu-doped goethite is supported by the release of Cu from the solid as a function of pH as shown in Figure 4.32 (B). It is evident from this Figure that with increasing pH the trend of Cu release is similar to Fe for this sample of goethite. Further, it has been reported in the literature that oxyanions like chromate and arsenate, inhibit dissolution of goethite (Eick et al., 1999). But in our case this is true only for pure goethite. In case of Cu-doped goethite, chromate concentration has no effect on dissolution of Cu-doped goethite. This behavior of Cu-doped goethite is evident from the plot of Cu released as a function of chromate concentration, given in Figure 4.32 (C). Moreover, dissolution of pure and Cu-doped goethite was also studied in 0.01, 0.1 and 0.5MKNO₃ and the results are shown in Figure 4.33 (A), (B) and (C), which shows that dissolution of Cu-doped goethite increases with increasing concentration of KNO₃, while the reverse is true for pure goethite. Therefore, it can be inferred from this discussion that the enhanced dissolution of Cu-doped goethite at pH 3 is due to the presence of Cu in the solid which leaches easily in acidic condition. In the presence of chromate solutions containing 0.1M KNO₃ as a background electrolyte, no iron was found in the solution for both the samples of goethite, suggesting that it is precipitated over the adsorbed chromate on the surface of goethite according to the mechanism proposed by Hongshao and Stanforth, (2001) for the adsorption of phosphate and arsenate on the surface of goethite.
Figure 4.32  (A) Iron release as a function of pH from pure and Cu-doped goethite in 0.1 MKNO$_3$ at 303K, (B) Cu release from Cu-doped goethite in 0.1MKNO$_3$ and (C) Cu release from Cu-doped goethite as a function of chromate concentration at 303K.
Figure: 4.33 (A) and (B) Iron release as a function of pH from pure and Cu-doped goethite respectively, in different concentrations of MKNO₃ at 303K, (C) Cu release from Ni-doped goethite in different concentrations of MKNO₃ at 303K.
4.3.3 Adsorption Studies

Chromate adsorption on both pure and Cu-doped goethite was investigated in the temperature range 303-323K at pH 3, 5 and 7. The findings of the studies are discussed in detail bellow.

4.3.3.1 Effect of pH

Sorption isotherms for pure and Cu-doped goethite are shown in Figure 4.34 (A) and (B), where it can be seen that the sorption of chromate is highly pH-dependent and decreases with increasing pH. The increase in chromate sorption with decreasing pH is due to the pH-dependent nature of chromate species and decrease in the magnitude of positive charge on surface of goethite with increasing pH according to equations 4.2 and 4.3.

At pH 3 the surface of goethite is protonated according to equation (4.2) and hence, favors the sorption of negatively charged chromate anion (HCrO$_4^-$), which is the dominant chromate species in the pH range 2-7 (Erdem et al., 2004). Further, it can be noted from the isotherms that under the same experimental conditions, Cu-doped goethite adsorb greater amount of chromate as compared to pure goethite. For comparing the sorption capacities, a plot of pH vs amount of chromate sorbed (%) by both the samples of goethite is given in Figure 4.34 (C). It is evident from this Figure that adsorption capacity of goethite is increased significantly with Cu$^{2+}$ ions doping. At pH 3, where maximum amount of chromate is adsorbed, the adsorption capacity of pure goethite is 64.4%, while that of Cu-doped goethite is 84.5%. The increase in % adsorption of Cu-doped goethite may be due to the greater surface area and pore volume of this sample of goethite. Moreover, small amount of chromate may also be precipitated at pH 3 according to the mechanism discussed in 4.3.2, which may also contribute to the enhanced capability of the Cu-doped solid to remove chromate form the solution phase.

4.3.3.2 Effect of Temperature

Figure 4.35 (A) and (B) show the effect of temperature on the sorption of chromate by pure and Cu-doped goethite respectively, where it is evident that by increasing the temperature chromate uptake increases in case of pure goethite while it decreases in case of Cu-doped
goethite. By increasing the temperature from 303 to 323K at pH 3, the % adsorption of chromate by pure goethite increases from 64.3 to 75.4%, while the same increase in temperature causes the % adsorption of chromate by Cu-doped goethite to decrease from 84.5 to 71.01%. These results show that the process of adsorption is endothermic in case of pure goethite and exothermic in case of Cu-doped goethite. Both endothermic and exothermic adsorption of oxyanions had been reported in the literature (Erdem et al., 2004; Mallick et al., 2006).
Figure: 4.34 Sorption Isotherms for chromate (A) pure goethite and (B) Cu-doped goethite at 303K. (C) Comparison of chromate anions sorbed (%) by pure and Cu-doped goethite as a function of pH at 303K, using 0.83mmol/L of chromate solution (Suspension density: 5mg/ml).
Figure: 4.35  Amount of chromate sorbed at pH 3 by (A) pure goethite and (B) Cu-doped goethite at different temperatures (Suspension density: 5mg/ml).
4.3.4 Adsorption Isotherm

Langmuir adsorption isotherm in the linear form as given in equation 4.8 was found applicable to the experimental data and the best fit of this equation is shown in Figure 4.36 (A) and (B). The plots are linear with R² values in the range 0.96 to 0.99 at all the pH values. The values of Langmuir constants Xₘ and Kₜ were calculated by applying equation (4.8) to the data in the temperature range 303-323K and pH values 3, 5, 7 and are given in Table 4.10. It can be noted from the Table that the values of Xₘ are fairly larger for Cu-doped goethite as compare to the pure goethite sample, showing the enhanced chromate removal capacity of this goethite sample, which agrees well with the results given in Figure 4.34 (C). The values of Kₜ are also larger for Cu-doped goethite, which show that chromate sorbs more firmly to the surface of this goethite sample as compare to pure goethite. Similar increase in the values of Langmuir constants for Cu-doped goethite was reported by Mohapatra et al., (2006).

4.3.5 Isosteric Heat of Adsorption

Isosteric heats for the adsorption of chromate on both the samples of goethite were determined from Clausius Clapyron Equation, given in equation 4.9. The values of $\Delta H$ are given in Table 4.11, which were calculated from the plots of $\ln(Ce(r)) \, vs \, \frac{1}{T}$ as shown in Figure 4.37 (A) and (B). It can be noted from the table that the values of $\Delta H$ are positive for pure goethite and negative for Cu-doped goethite, showing that process of adsorption is endothermic in case of pure goethite and exothermic in case of Cu-doped goethite. The decrease in the vales of $\Delta H$ with increasing surface coverage is due to the surface heterogeneity (Choudhary et al., 1988) and is in agreement with the results of Sharma (2001) for chromate adsorption on Wollastonite. The exothermic nature of chromate adsorption on Cu-doped goethite is probably due to the greater capacity of this sample of goethite to adsorb H⁺/OH⁻ ions as is evident from Figure 4.27. The sorption of H⁺ ions on the surface of goethite is exothermic to the extent of -58 KJmol⁻¹ as reported by Angove et al. (1999).
4.3.6 FTIR Analysis

Figure 4.31 (spectrum C), shows the IR spectrum of Cu-doped goethite sample, which was treated with 0.83 mmol/L chromate solution at pH 3 and 303K for 24 hours. Comparing this spectrum (C) with the spectrum of the as used Cu-doped goethite (spectrum B), it can be seen the broad and intense NO$_3^-$ band at 1382 cm$^{-1}$, evident in spectrum (B), almost disappears after treatment of the solid with chromate. Similarly, the band at 1531 cm$^{-1}$ in spectrum B, which is reported to be due to the split $\nu_3$ modes of surface carbonates (Karmakar et al., 2004), also disappears in spectrum C. These changes suggest that the surface NO$_3$ and CO$_3^{2-}$ are exchanged at the solid-solution interface. The CrO$_4^{2-}$ group stretching mode vibrations occurring in the 770-1000 cm$^{-1}$ absorption range (Repka et al., 1998) seems to have been masked by the strong absorption bands of OH bending vibrations, which also occurs in this absorption region.

4.3.7 Mechanism of the Reaction

From the FTIR analysis it becomes clear that the HCrO$_4^-$ species is adsorbed to the solid surface through ion exchange mechanism by replacing surface NO$_3^-$, CO$_3^{2-}$ and OH$^-$ groups at pH-5 and 7, according to the following reactions;

\[
\begin{align*}
&MNO_3 + HCrO^- \rightarrow MHCrO_4 + NO_3^- \quad (4.16) \\
&M_2CO_3 + 2HCrO^- \rightarrow 2MHCrO_4 + CO_3^{2-} \quad (4.17) \\
&MOH + HCrO^- \rightarrow MHCrO_4 + OH^- \quad (4.18)
\end{align*}
\]

where M represents the anion bonded metal surface, which may be Fe or Cu. As most of the goethite surface is hydroxylated, therefore reaction (4.18) seems to be the dominant surface reaction resulting in the increase in equilibrium pH at pH 5 and 7 as can be seen from Table 4.12. However, as the table reveals that the increase in chromate sorption is not accompanied by the expected increase in equilibrium pH, which may be the result of the OH$^-$ consumption in the precipitation of the corresponding Cu(OH)$_2$, released according to reaction (4.18). This
is in agreement with the data given in Figure 4.30 (C), where the Cu release from the surface is observed to be independent of the chromate concentration. The Table also shows that the equilibrium pH remains constant at pH 3 and is almost independent of chromate sorption. This again, may also be due to the interaction of OH\(^-\) anions with Cu\(^{2+}\) ions.
Figure: 4.36 Langmuir plots for adsorption of chromate by (A) pure goethite and (B) Cu-doped goethite (Suspension density: 5mg/ml).
Figure: 4.37 Plot of Clausius clapeyron equation at pH 3 for (A) pure and (B) Cu-doped goethite.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
<th>Fe (%)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Goethite</td>
<td>34.69</td>
<td>0.02</td>
<td>62.4</td>
<td>-</td>
</tr>
<tr>
<td>Cu-doped Goethite</td>
<td>126.52</td>
<td>0.006</td>
<td>60.8</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Table: 4.9**  
Surface characteristics and chemical composition of pure and Cu-doped goethite.

<table>
<thead>
<tr>
<th>pH</th>
<th>Pure Goethite</th>
<th>Cu-doped Goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xₚ</td>
<td>Kᵇ</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>11.44</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>17.82</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>2.96</td>
</tr>
</tbody>
</table>

**Table: 4.10**  
Langmuir constants Xₚ (mmol.g⁻¹) and Kᵇ (L.mmol⁻¹) for pure and Cu-doped goethite at 303K.
<table>
<thead>
<tr>
<th>Pure goethite</th>
<th>Cu-doped goethite</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>pH 5</td>
</tr>
<tr>
<td>(X)</td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>0.04</td>
<td>51.15</td>
</tr>
<tr>
<td>0.06</td>
<td>28.20</td>
</tr>
<tr>
<td>0.08</td>
<td>10.65</td>
</tr>
<tr>
<td>0.1</td>
<td>13.67</td>
</tr>
<tr>
<td>0.12</td>
<td>3.13</td>
</tr>
</tbody>
</table>

**Table: 4.11** Changes in \(\Delta H\) values (KJmol\(^{-1}\)) with increasing surface coverage ‘X’ (mmol.g\(^{-1}\)) for chromate adsorption on pure and Cu-doped goethite at 303K.

<table>
<thead>
<tr>
<th>Initial Cr(VI) Concentration (mmol.L(^{-1}))</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
<th>pH 3</th>
<th>pH 5</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure goethite</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
</tr>
<tr>
<td>Cu-doped goethite</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
<td>(pH_i)</td>
<td>(pH_f)</td>
</tr>
<tr>
<td>0.22</td>
<td>2.98</td>
<td>2.92</td>
<td>5.02</td>
<td>5.52</td>
<td>6.97</td>
<td>7.21</td>
</tr>
<tr>
<td>0.50</td>
<td>3.04</td>
<td>2.87</td>
<td>5.04</td>
<td>5.64</td>
<td>6.98</td>
<td>7.13</td>
</tr>
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<td>2.95</td>
<td>2.91</td>
<td>5.01</td>
<td>5.77</td>
<td>6.98</td>
<td>7.10</td>
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<td>1.02</td>
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<td>2.88</td>
<td>4.98</td>
<td>5.43</td>
<td>7.00</td>
<td>7.22</td>
</tr>
<tr>
<td>1.17</td>
<td>2.96</td>
<td>2.88</td>
<td>5.02</td>
<td>5.45</td>
<td>6.97</td>
<td>7.24</td>
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<td>4.99</td>
<td>5.40</td>
<td>7.00</td>
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<td>1.55</td>
<td>2.98</td>
<td>2.89</td>
<td>5.03</td>
<td>5.35</td>
<td>6.97</td>
<td>7.20</td>
</tr>
</tbody>
</table>

**Table: 4.12** Changes in equilibrium pH of pure and Cu-doped goethite suspensions in various concentrations of chromate at 303K.
4.4 Characterization and Chromate Adsorption Properties of Cu-doped Goethite and Amorphous Copper and Iron Mixed Oxides

It is interesting to note that doping of each metal(II) ion, considered in the present investigation, has a pronounced effect on the chromate adsorption capacity of goethite. The amount of chromate sorbed by each sample as a function of pH is shown in Figure 4.38, which shows that the chromate adsorption capacity of the adsorbents decreases in the following order;

Cu-doped goethite > Ni-doped goethite > Pb-doped goethite > pure goethite

Thus, due to the promising behavior of the Cu-doped goethite for the adsorption of chromate, the copper contents of the Cu-doped solid were increased form 0.32% to 11.31%, in order to determine the behavior of goethite when it contains higher concentration of copper. It’s worth mentioning here, that the maximum amount of copper, which can be incorporated into the goethite crystals, is not more than 3% (Inouye et al. 1972; Huynh et al. 2002). Beyond this limit, it is reported to retard completely the crystallinity of goethite, resulting in the formation of amorphous phases iron and copper oxides. Similar, results were obtained in the present study by increasing the copper contents of the solid phase from 0.32% to 11.31%. However, in line with the main interest of the present investigation, two more samples were prepared containing 6.27 and 11.31% copper. The characteristics and adsorption properties of these samples towards chromate are reported here following the nomenclature given in the beginning of this chapter.
Figure: 4.38  Comparison of chromate sorption capacity (%) of pure, Pb, Ni and Cu-doped goethite as a function of pH, using 0.8 mmol/L chromate solution at 303K (Suspension density; 5mg/ml).
4.4.1 Characterization

Surface area and chemical composition of the hydrated mixed oxides are given in Table 4.13, showing that surface area increases significantly by increasing the Cu contents of the solids. The increase in surface area may be due to the exchange of Fe by Cu from aqueous solution, as the latter has a greater ionic radius of 0.73 Å as compared to the former 0.645 Å. It can be seen from Figure 4.39 that the Cu-doped sample with lowest Cu content is crystalline and shows all the characteristic d-spacing values of goethite (α-FeOOH) (Abdel-Samad, and Watson; 1998), while the other two samples are amorphous. Due to its amorphous nature, the hydrated oxide sample with highest Cu content has the largest surface area. Changes in morphologies of the solid particles of all the samples can be seen more clearly from their SEM images, shown in Figure 4.40. These images suggest that the solid sample HMO-I, having the lowest copper contents has typical needle like crystals of goethite (Kosmulski, et al. 2004). The sample HMO-II consists of smaller goethite crystals, along with some amorphous phases, while the sample HMO-III is completely amorphous in nature. Similar effect of copper doping on the properties of iron oxide has been reported by a number of authors (Inouye et al. 1972; Huynh et al. 2002; Mohapatra et al. 2006).

Figure 4.41 shows FTIR spectra of the hydrated mixed oxides samples, where characteristic bands of goethite at 636, 792 and 894cm⁻¹ are evident in the IR spectrum of sample HMO-1 (spectrum A). In this spectrum the band at 636cm⁻¹ is due to Fe-O symmetric stretching (Lakshmipathiraj et al. 2006) and the bands at 793 and 894cm⁻¹ are due to OH bending vibrations (Cambier, 1986). Spectrum B represents the FTIR spectrum of sample HMO-II, which shows all the characteristic bands of goethite, but with significantly reduced intensity. These findings are in agreement with the SEM micrographs shown in Figure 4.40, which suggest that crystalline phase of goethite does exists in sample HMO-II but the crystals have a distorted geometry and are relatively
smaller in size. This change in the morphology of goethite crystals seems to be due to the development of Cu(OH)$_2$ phase in the solid, for which a shoulder is evident in the absorption region of 450-550 cm$^{-1}$ in the FTIR spectrum of HMO-II (Jagminas et al.).

FTIR spectrum of sample HMO-III, shown in Figure 4.40 (C), bears a clear band for Cu(OH)$_2$ along with a broad band in the absorption region of 600-900 cm$^{-1}$. This band seems to be a cluster of peaks for CuO occurring at 820, 596, 538 and 501 cm$^{-1}$ (Guedes et al. 2009) and bands for Fe-O and OH stretching and bending vibrations. The bands at 1382/1380 cm$^{-1}$, in all the spectra are assigned to NO$_3^-$ group (Hu et al. 2007), while the IR bands between 3000-3600 and 1650 cm$^{-1}$ in all the spectra are due to hydroxyl stretching and bending mode of vibrations respectively (Boily et al. 2006). The band in 1500-1550 cm$^{-1}$ region in spectra A, B and C is probably due to the split $\nu_3$ vibrations of surface carbonates (Karmakar et al. 2004). These results, suggests that the sample HMO-I is acicular Cu-goethite, HMO-II is a mixed microcrystalline phase mainly consists of Cu-goethite with small amount of CuO and Cu(OH)$_2$, while the sample HMO-III is also a mixed phase, consisting of amorphous Fe(OH)$_3$, CuO and Cu(OH)$_2$.

Point of zero charge (pH$_{pzc}$) of the hydrated mixed oxides is shown in Figure 4.42, where it can be observed that the value of PZC increases with increasing the Cu contents in the solids. This may be due to the increased formation of the Cu oxide/hydroxide phases in the solid as suggested earlier. As Cu(OH)$_2$ has a larger PZC value of about 7.9 (Guedes et al. 2009), therefore, its presence in the composite oxide results in the increase of the average pH$_{pzc}$ value. Similar conclusions have been made by many authors for metal-doped iron oxides (Zhang et al. 2003).
Figure 4.39  XRD patterns of the hydrated mixed oxide samples.
Figure 4.40  SEM images (A) HMO-I (B) HMO-II (C) HMO-III.
Figure 4.41 FTIR spectra of the as used HMO-I (A), HMO-II (B) and HMO-III (C) and chromate treated HMO-III (D).
Figure 4.42  pH of point of zero charge and for the hydrated mixed oxide samples in 0.1M KNO₃ at 303K.
4.4.2 Adsorption Studies

pH edges for chromate adsorption on all the solid samples in 0.63 and 1.8 mmol.L\(^{-1}\) chromate solutions are shown in Figure 4.43 (A) and (B) respectively. It can be seen clearly from them that the amount of chromate sorbed by all the solids decreases drastically with increasing pH. The steepness of the chromate adsorption edges is reported to be due to the protonation of the chromate anion and is in agreement with the results of Eick et al. (1999). It can also be noted from this Figure that the amount of chromate adsorption increases with the increase in Cu contents of the solid, which as discussed earlier, is due to the increase in surface area of the solid on account of Cu(OH)\(_2\) formation on the surface. Further the decrease in adsorption with the increase in pH is due to the decrease in the magnitude of positive charges on the surface of iron oxides according to the equilibria shown in equation 4.2 and 4.3. As the dominant species of chromate between pH 2-7 is HCrO\(_4^-\) (Erdem et al., 2004), therefore, it can be assumed that that its adsorption is favored at lower pH.

The increase in the amount of chromate adsorption with increase in copper content of the solid, is due to the presence of Cu(OH)\(_2\)/CuO on the surface of the solid. it exists in the form of CuOH\(^+\) below its PZC, which is reported by Guedes et al. (2009) to be about 7.9. Therefore, its presence on the surface increases the magnitude of positive charge at lower pH values. Similarly, the increase in the surface area, which increases with increasing Cu contents of the solid, may also has a major contribution to the increase in the adsorption of chromate.

Due to the adsorption maxima shown by all the solids at pH 3, under the experimental conditions of the present study, adsorption studies for all the samples were carried out at pH 3 and 303K, using different concentrations of chromate and the resultant adsorption isotherms are shown in Figure 4.44 (A). The data in this Figure show that the sample HMO-III has the highest chromate adsorption capacity of all the samples investigated. It
can also be seen from this Figure that under the given experimental conditions the sorption capacity of the sample HMO-III is almost tripled as compared to sample HMO-I.

The Langmuir isotherm model was found applicable to the data in its linear form shown in equation 4.8 and the plots of this equation are shown in Figure 4.44 (B), which are linear with $R^2$ values in the range 0.95 to 0.98. The values of $X_m$ and $K_b$ obtained from the Langmuir plot i.e. Figure 4.44 (B), are given in Table 4.14, where it is evident that the values of both $X_m$ and $K_b$ increases with increasing the quantity of copper in the solid phase and the sample HMO-III has the maximum $X_m$ and $K_b$ values, showing its enhanced sorption capacity and firm bonding of chromate anions among all the samples under investigation. Due to the promising behavior of this sample for chromate adsorption, its dissolution and sorption behavior as a function of temperature was also investigated.
Figure 4.43  pH edges for the hydrated mixed oxide samples using (A) 0.63 mmol/L and (B) 1.8 mmol/L chromate solutions at 303K (Suspension density; 5mg/ml).
Figure 4.44  Sorption isotherms (A) and Langmuir plot (B) for the mixed oxide samples at pH 3 and 303K (Suspension density; 5mg/ml).
4.4.3 Dissolution of the sample HMO-III

Iron release as function of pH in 0.1M KNO₃ form HMO-III is shown in Figure 4.45 (A), where it is evident that at lower pH values the iron containing phase dissolves significantly. However, as the pH value increases above 5, no iron is detected in the solution phase. Similar trend in Figure 4.45 (B) is observed for the copper release from the solid in 0.1M KNO₃ and 1.8 mmol.L⁻¹ chromate solution. It can also be noted from this Figure that the amount of copper released from the solid is comparatively greater than iron under similar experimental conditions. The dissolution of metal doped iron oxides due to proton attack in acidic conditions is well documented in the literature (Alvarez et al. 2006; Huynh et al. 2002). The dissolution trend given in Figure 4.45 (A) and (B), if compared with the adsorption behavior of the solid given in Figure 4.44 (A), leads to the conclusion that HMO-III is a promising adsorbent at the pH value of 5 and above, where it is not only stable but is very selective to remove the chromate.

4.4.4 Effect of Temperature on the adsorption of chromate by the sample HMO-III

The effect temperature on chromate adsorption by the sample HMO-III was investigated using different concentrations of chromate and the results are shown in Figure 4.46 (A). It can be seen from this Figure that adsorption of chromate increases with increasing the temperature of the system. The increase in adsorption with increasing temperature shows endothermic nature of the adsorption process (Erdem et al., 2004). By comparing the data with Figure 4.44 (A), it can be noted that the amount of chromate adsorbed by this sample at pH 5 and 323K is about 0.3mmol/g, which exceeds the amount of chromate adsorbed by the other two samples even at pH 3.

Isosteric heats of adsorption for chromate adsorption for the sample HMO-III, were calculated from the plot of \( \ln Ce(r) \) vs \( \frac{1}{T} \), as shown in Figure 4.45 (B), using the well known Clausius Clapyron Equation given in equation 4.9. The changes in the values of
$\Delta H$ with increasing surface coverage are given in Table 4.15, which show that these values gradually decrease with increasing the surface coverage. The decrease in the values of $\Delta H$ with increasing surface coverage is due to the surface heterogeneity (Choudhary et al., 1988) as the high energy surface sites are occupied first leaving behind the lower energy sites. The results are in agreement with the results of Sharma (2001) for chromate adsorption on Wollastonite.

4.4.5 Mechanism of the Reaction

The FTIR spectrum (D) for HMO-III, given in Figure 4.41, shows that the bands in the original spectrum (Figure 4.41 C), at 450-600, and 550-900 cm$^{-1}$, disappear and a weak band appears in the 400-700 cm$^{-1}$ region. These results suggest that after treatment of the solid with 1.8 mmol.L$^{-1}$ of chromate solution the $\nu_1$-$\nu_3$ modes of Cr-O vibrations of the chromate appear in the range of 400-900 cm$^{-1}$ due to the formation of innersphere complexes in the system (Baron et al.). The band in 1500-1550 cm$^{-1}$ region in the as used spectrum, which is due to the split $\nu_3$ modes of surface carbonates, disappears and a relatively weaker new band appears at about 958 cm$^{-1}$. This band seems to be due to the splitting of Cr-O stretching mode, which is reported to occur in the 770-1000 cm$^{-1}$ range (Repka et al., 1998), suggesting the presence of coordinated $\text{CrO}_4^{2-}$ group on the surface.

The changes in equilibrium pH of the suspensions with chromate adsorption at the lowest and highest temperature are given in Table 4.16, where a considerable increase in pH after the establishment of the equilibrium is observed. The increase in the equilibrium pH of the suspension clearly indicates that adsorption of the anion results in releasing OH$^-$ ions to the solution phase. From the foregoing discussion, it can be concluded that the dominant uptake mechanism for chromate anion by the solid is innersphere complexation, removing $\text{CO}_3^{2-}$ and OH$^-$ ions from the surface according to the following reactions

$$= \text{MOH} + H\text{CrO}_4^- \rightarrow M\text{HCrO}_4 + \text{OH}^-$$

(4.19)
\[ M_2CO_3 + 2HCrO_4^- \rightarrow 2MHCrO_4 + CO_3^{2-} \] (4.20)

where M represents the anion bonded metal surface, which, in the present case may be Fe or Cu. As most of the iron oxide surface is hydroxylated, therefore reaction (4.19) seems to be the dominant surface mechanism for the sorption of chromate by HMO-III. The proposed mechanism is consistent with the results of Hu et al. (2005) for the adsorption of chromate on Maghemite nanoparticles. They suggested that at lower pH value of 2.5 the dominant mechanism of chromate adsorption is outersphere complexation, while at the pH value of 8 the reaction mechanism is completely changed to innersphere complexation.
Figure 4.45  (A) Iron release from HMO-III as a function of pH in 0.1M KNO$_3$ and 303K and (B) Cu release from HMO-III as a function of pH at 303K.
Figure 4.46  (A) Effect of temperature on chromate sorption by the mixed oxide sample HOM-III at pH-5, (B) Plot of Clausius Clapeyron equation for chromate sorption by the mixed oxide sample HOM-III at pH-5 (Suspension density; 5mg/ml).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m$^2$ g$^{-1}$)</th>
<th>pH$_{pzc}$</th>
<th>Fe (%)</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMO-I</td>
<td>126.5</td>
<td>7.30</td>
<td>60.8</td>
<td>0.32</td>
</tr>
<tr>
<td>HMO-II</td>
<td>224.3</td>
<td>7.50</td>
<td>54.3</td>
<td>6.27</td>
</tr>
<tr>
<td>HMO-III</td>
<td>261.2</td>
<td>7.70</td>
<td>49.7</td>
<td>11.31</td>
</tr>
</tbody>
</table>

Table: 4.13  Surface characteristics and chemical composition of the hydrated mixed oxide samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$X_m$</th>
<th>$K_b$</th>
<th>$R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMO-I</td>
<td>0.21</td>
<td>29.46</td>
<td>0.998</td>
</tr>
<tr>
<td>HMO-II</td>
<td>0.36</td>
<td>17.98</td>
<td>0.966</td>
</tr>
<tr>
<td>HMO-III</td>
<td>0.44</td>
<td>49.31</td>
<td>0.995</td>
</tr>
</tbody>
</table>

Table: 4.14  Langmuir constants $X_m$ (mmol.g$^{-1}$) and $K_b$ (L.mmol$^{-1}$) at pH 3 and 303K for the hydrated mixed oxide samples.

<table>
<thead>
<tr>
<th>X</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>39.78</td>
</tr>
<tr>
<td>0.15</td>
<td>35.58</td>
</tr>
<tr>
<td>0.2</td>
<td>34.28</td>
</tr>
<tr>
<td>0.25</td>
<td>30.82</td>
</tr>
<tr>
<td>0.3</td>
<td>36.42</td>
</tr>
</tbody>
</table>

Table: 4.15  Changes in $\Delta H$ values (KJmol$^{-1}$) with increasing surface coverage ‘X’ (mmol.g$^{-1}$) for HMO-III at pH 5.
<table>
<thead>
<tr>
<th>Initial Cr(VI) Concentration (mmol.L⁻¹)</th>
<th>303K</th>
<th>323K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pHᵢ</td>
<td>pHᵢ</td>
</tr>
<tr>
<td>0.22</td>
<td>4.99</td>
<td>5.98</td>
</tr>
<tr>
<td>0.50</td>
<td>5.02</td>
<td>6.06</td>
</tr>
<tr>
<td>0.78</td>
<td>5.01</td>
<td>5.97</td>
</tr>
<tr>
<td>1.02</td>
<td>4.97</td>
<td>5.92</td>
</tr>
<tr>
<td>1.17</td>
<td>5.01</td>
<td>6.11</td>
</tr>
<tr>
<td>1.43</td>
<td>4.98</td>
<td>5.78</td>
</tr>
<tr>
<td>1.55</td>
<td>4.96</td>
<td>6.12</td>
</tr>
</tbody>
</table>

**Table: 4.16** Changes in equilibrium pH with increasing temperature after treatment of the sample HMO-III with chromate solutions of different concentrations at pH 5.
4.5 Comparative Account of the Physico-chemical Properties and Chromate Adsorption Behavior of Metal-doped Goethites and Mixed Oxides of Iron and Copper

4.5.1 Surface Area and Pore Volume

Surface area and pore volumes are important parameters in determining the sorption behavior of any adsorbent. In the present study, it can be noted that in general all the metal cations significantly increase the surface area of goethite. However, the extent of increase varies for different cations, such as Pb$^{2+}$ doping causes the least increase while Cu$^{2+}$ causes the maximum increase in the surface area of goethite. As far as the pore volume is concerned, it is decreased by the Pb$^{2+}$ ion, while significantly increased by Ni$^{2+}$ and Cu$^{2+}$ ions presence in goethite crystals. These effects are mainly due to the difference in the ionic radii of the doped metals and iron as discussed in their respective sections in detail earlier.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m$^2$ g$^{-1}$)</th>
<th>Pore Volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Goethite</td>
<td>34.69</td>
<td>0.02</td>
</tr>
<tr>
<td>Pb-doped Goethite</td>
<td>77.80</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni-doped Goethite</td>
<td>125.99</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu-doped Goethite</td>
<td>126.52</td>
<td>0.006</td>
</tr>
<tr>
<td>HMO-II</td>
<td>224.3</td>
<td>7.50</td>
</tr>
<tr>
<td>HMO-III</td>
<td>261.2</td>
<td>7.70</td>
</tr>
</tbody>
</table>

Table: 4.17  Surface characteristics and chemical composition of pure and Pb-doped goethite.
4.5.2 Point of Zero Charge (pH\text{pzc})

All the doped metal ions cause very slight increase in pH\text{pzc} or have no effect on this property of goethite. The increase in the pH\text{pzc} values of the solids is due to the development of the solid into a composite oxide and has been reported that the point of zero charge of a composite oxide is approximately the weighted average of the values of its components (Stumm, 1992). It can be seen from Figure 4.47 that Cu-goethite has the same pH\text{pzc} as that of pure goethite while the highest copper containing mixed oxide has the highest pH\text{pzc} value of all the solids with an increase of approximately one pH unit, suggesting the small effect of copper doping on the pH\text{pzc} of the solids. However, as discussed in the earlier sections, it is interesting to note that the presence of foreign elements in the iron oxide cause a relative increase in their ΔpH values as compare to pure goethite. In case of metal-doped goethites the increase in ΔpH values is due to the formation of doped metal oxide/hydroxide on the surface of the solid which increases their H⁺/OH⁻ adsorption capacity. While the increase in the H⁺/OH⁻ adsorption capacity of mixed oxides of copper and iron is due to their increased surface area. However, with the increase in the copper content of the iron oxide depress the ΔpH values, which exactly follow the order of decreased crystallinity of the solid.
Figure 4.47  Point of Zero Charge for pure Pb, Ni, Cu-doped goethites and Mixed oxides of iron and copper in 0.1M KNO$_3$ at 303K.
4.5.3 Crystallinity

It has been reported that the isomorphic substitution of metal ions for Fe can be done within the limit of a specific metal to Fe ratio and beyond this limit the crystal structure of goethite is depressed and retarded, resulting in the formation of phases other than goethite. However, within the limit of its doping, each metal has a pronounced effect on the physical and chemical properties of goethite (Gerth, 1990). It can be observed from the XRD spectra given in Figures 4.3, 4.15, 4.28 and 4.39, that the Pb, Ni, and Cu-doped goethites are crystalline in nature, while the samples HMO-II and HMO-III are amorphous. These observations suggest that as long as the concentration of doped metal is within the limit of its doping, the crystallinity of the solid remains intact, while crossing this limit deforms the crystal structure of the solid as observed in case of HMO-II and HMO-III. These observations are further supported by the TEM/SEM images given in Figures 4.4, 4.17, 4.30 and 4.40, which show that the Pb, Ni, and Cu-doped goethites have acicular crystals, typical of goethite, while the samples HMO-II and HMO-III are microcrystalline and amorphous in nature respectively. The images further reveal that doping of small amounts of these metals not only increases the width and length of crystals, but also causes a slight roughness of the solid surface due to the production of sub-grain boundaries in it.

4.5.4 Thermogravimetric Behavior

Thermogravimetric analysis of the metal doped goethite, given in Figures 4.2, 4.16 and 4.28, suggest that below 500°C the doped goethites show weight losses similar to pure goethite with slight variations due to the removal of physically adsorbed water, hydroxyl groups and the topotactic transformation of goethite to hematite. However, above 500°C, the metal-doped goethites show significant weight losses with broad endothermic peaks. These weight losses are different for different doped metals, such as 9.22% for Pb 3.279%
for Ni and 1.44% for Cu. All these weight losses are due to the deformation of the respective doped metal hydroxides to form the metal oxides and decomposition of $NO_3^-$ ions present in the solid as an impurity. In case of the mixed oxides of iron and copper the Thermogravimetric analyses of HMO-II and HMO-III have not been included here due to the presence of two separate phases in the solid. These two phases loses weights separately and independent of each other right from the beginning of the thermal analyses and hence do not depict any distinct feature of the solid.

**4.5.5 Dissolution**

After getting through the dissolution data for all the solids, it becomes clear that all the solids considered in this study are dissolved significantly at the lowest pH value of 3, while increasing the pH decreases their dissolution to varying degrees in different samples. Iron released from the pure and metal doped goethites is shown in Figure 4.48, which suggests that Pb-goethite is more readily dissolved in 0.1M KNO$_3$ as compared to any other of the solid samples, even the pure goethite. Its dissolution gradually decreases with increasing pH, which is also evident from the Figure. This behavior of Pb-goethite is due to the large size of Pb$^{2+}$ ion as compared to Fe$^{3+}$, which, when present in the crystals of goethite, causes a significant distortion in its crystal structure. The Ni and Cu-doped goethites show almost similar dissolution behavior at pH 3. However, by increasing the pH only by one unit the solid show far greater stability than pure and Pb-goethite under the same experimental conditions. This trend of dissolution in Ni and Cu-doped is due to their relatively smaller ionic sizes and hence better fitting into the crystal structure of goethite. It is also interesting to note that Cu-doped goethite is the most stable of all the goethite samples at pH 4 and above (Figure 4.48). Hence, following the dissolution inhibition effect of Cu$^{2+}$ the sample HMO-III shows very little dissolution at pH 4 and gain complete stability at pH 5 and above.
Figure 4.48  Iron release as a function of pH from pure Pb, Ni, and Cu-doped goethites in 0.1M KNO$_3$ at 303K.
4.5.6 Adsorption of Chromate

Adsorption of chromate by all the solid samples has been investigated in the temperature 293-303K at pH 3, 5 and 7. It has been observed that adsorption of chromate decreases with increasing pH, due to decrease in the surface positive charge of the solid. However, the amount adsorbs per unit mass of the solid at constant pH is different for different solids. The general trend of increasing chromate adsorption exhibited by the different samples considered in the present investigations is as follows:

HMO-III > HMO-II > Cu-doped goethite > Ni-doped goethite > Pb-doped goethite > pure goethite. The effect of temperature upon the adsorption of chromate by these solids is, however, different for different samples. In case of HMO-III, Ni-doped goethite and pure goethite chromate adsorption increases with increasing temperature, while it decreases in Cu and Pb-doped goethites.

The data of chromate adsorption strictly follow Langmuir model of adsorption at all the experimental conditions considered in the present investigation. Langmuir constants calculated from the adsorption data are given in Table 4.18, which suggest that the sample HMO-III has the largest $X_m$ value showing that this solid has the largest adsorption capacity for chromate, while pure goethite has the least. The binding energy constant $K_b$ values given in this Table show that sample HMO-III has the highest $K_b$ value which is followed by the Pb-doped goethite. It is interesting to note that in spite of the low $X_m$ value, the $K_b$ value of Pb-doped goethite is the largest after HMO-III, which suggests that chromate is more firmly adsorbed by this sample of goethite as compared to pure, Ni and Cu-doped goethites.

Isosteric heats of adsorption have been calculated by using Clausius Clapyron and the Changes in its values with increasing surface coverage for all the samples are given in Table 4.19. This Table shows that the values of isosteric heat of adsorption are consistent with the endothermic/exothermic nature of the surface reactions. In case of endothermic
process of adsorption like in pure, Pb and HMO-III, the values of isosteric heats of adsorption are positive, while in the exothermic process of adsorption these values are negative like in Pb and Cu-doped goethite. Except Ni-doped goethite, in all the other samples the values of $\Delta H$ decreases with increasing surface coverage due to heterogeneity of the surface. In case of Ni-doped goethite doped goethite, the increase in the values of $\Delta H$ with increasing surface coverage is, however, due to the increased sorbate-sorbate interaction on surface of this solid.

Keeping in view the all the experimental evidences present in the earlier sections, it can be concluded that mechanism of the chromate adsorption is similar for all the solid samples. At the lowest pH of 3 the dominant mechanism is outer surface complexation, which can be represented by the following reaction scheme;

$$MOH_2^+ + HCrO_4^- \rightarrow MOH_2^+ - HCrO_4^-$$ (4.21)

However, at pH 5 and 7 mechanism of the surface reaction is changed from outer to inner sphere complexation, which involves the removal OH$, NO_3^-$ and CO$_3^{2-}$ from the solid as;

$$= MNO_3 + HCrO^- \rightarrow MHCrO_4 + NO_3^-$$ (4.22)

$$= M_2CO_3 + 2HCrO^- \rightarrow 2MHCrO_4 + CO_3^{2-}$$ (4.23)

$$= MOH + HCrO^- \rightarrow MHCrO_4 + OH^-$$ (4.24)

where M represents the anion bonded metal surface, which may be Fe or any one of the doped metals.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$X_m$</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMO-III</td>
<td>0.44</td>
<td>49.31</td>
</tr>
<tr>
<td>Cu-doped goethite</td>
<td>0.23</td>
<td>20.2</td>
</tr>
<tr>
<td>Ni-doped goethite</td>
<td>0.18</td>
<td>14.52</td>
</tr>
<tr>
<td>Pb-doped goethite</td>
<td>0.17</td>
<td>22.61</td>
</tr>
<tr>
<td>Pure goethite</td>
<td>0.14</td>
<td>11.44</td>
</tr>
</tbody>
</table>

Table 4.18 Langmuir parameters $X_m$ (mmolg$^{-1}$) and $K_b$ (Lmmol$^{-1}$) for different samples of goethite and amorphous mixed oxide of iron and copper at pH 3 and 303K.

<table>
<thead>
<tr>
<th>Pure goethite at pH 3</th>
<th>Pb-doped goethite at pH 3</th>
<th>Ni-doped goethite at pH 3</th>
<th>Cu-doped goethite at pH 3</th>
<th>Sample HMO-III at pH 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>$\Delta H$</td>
<td>X</td>
<td>$\Delta H$</td>
<td>X</td>
</tr>
<tr>
<td>0.04</td>
<td>51.15</td>
<td>0.06</td>
<td>-16.47</td>
<td>0.025</td>
</tr>
<tr>
<td>0.06</td>
<td>28.20</td>
<td>0.08</td>
<td>-16.51</td>
<td>0.05</td>
</tr>
<tr>
<td>0.08</td>
<td>10.65</td>
<td>0.10</td>
<td>-28.12</td>
<td>0.075</td>
</tr>
<tr>
<td>0.1</td>
<td>13.67</td>
<td>0.12</td>
<td>-34.44</td>
<td>0.1</td>
</tr>
<tr>
<td>0.12</td>
<td>3.13</td>
<td>0.14</td>
<td>-41.88</td>
<td>0.125</td>
</tr>
</tbody>
</table>

Table: 4.19 Changes in $\overline{\Delta H}$ values (KJmol$^{-1}$) with increasing surface coverage ‘X’ (mmol.g$^{-1}$) for chromate adsorption by pure, Pb, Ni and Cu-doped goethites and HMO-III at pH 3/5 and 303K.
Concluding Remarks

From the foregoing discussion it can be concluded that

1. Trace amounts of metal(II) ions can be incorporated into the crystals of goethite. The doped metal ions are present in the crystals of goethite as a substitute for Fe$^{3+}$ ions, causing very little changes in the morphology of goethite. In the present study, the 0.38% Pb$^{2+}$, 0.25% Ni$^{2+}$ and 0.32% Cu$^{2+}$ ions are present in hydroxylated form as a substitute for Fe$^{3+}$ ions in goethite. The spectroscopic data (XRD, TEM/SEM and FTIR) reveal that their isomorphous substitution for iron causes local distortion in the crystal structure of goethite due to (i) the compensation of charge imbalance between Fe$^{3+}$ and the divalent metal cation and (ii) difference in the ionic radii of Fe$^{3+}$ and the doped metal ion. These two factors go against the crystal development of goethite but they are counterbalanced by the relaxation and compliance effects to retain the basic framework of goethite structure.

2. The doping of Cu with increasing concentration reveals that crystal formation of goethite is retarded leading to the formation of amorphous phases. Thus, the 0.32% Cu containing solid is a typical crystalline goethite, while the solids, formed under similar experimental conditions, containing 6.27 and 11.31% copper are microcrystalline goethite and amorphous mixed iron and copper hydroxides.

3. The doping of 0.38% Pb$^{2+}$, 0.25% Ni$^{2+}$ and 0.32% Cu$^{2+}$ ions in goethite increases its surface area from 34.69 (pure goethite) to 77.80, 125.99 and 126.52 m$^2$.g$^{-1}$ respectively. In case when the amount of copper content of the solid sample increases from 0.32% to 11.31%, the surface area of the solid increases form 126.52 to 261.2 1 m$^2$.g$^{-1}$, due to the conversion of the solid phase from crystalline to completely amorphous.
4. pH_pzc of goethite increases from 7.25 to 7.45 with Pb and to 7.5 with Ni doping in goethite, while Cu doping upto 0.32% does not effect this property of goethite. However, by increasing the copper content of the solid phase up to 11.331%, the PZC value of the solid increases to 7.7. The increase in the pH_pzc values suggest that the solid after doping behave as a composite oxide of iron and the doped metal.

5. TG-DTA analysis show that in the temperature range 250-300°C, all the samples of goethite, considered in the present study, show thermal behavior of typical goethite with weight losses from 8-9%. However, each metal-doped goethite sample shows an additional weight loss in the temperature range 500-550°C, due to the dehydroxylation of the doped metal hydroxide and decomposition of NO_3^- anion present in the bulk of the solid.

6. Dissolution behavior of goethite, in terms of iron release shows that at the lowest pH value all the doped samples dissolve more readily than the pure goethite. However, with increasing pH, their dissolution is reversed and the metal-doped goethite samples become more stable than pure goethite. Further, in case of pure goethite increasing concentration of KNO_3 inhibits dissolution while in case of metal-doped goethites dissolution is promoted.

7. Chromate adsorption data show that that metal-doping results in an increase in its removal from aquous solutions following the order; HMO-III > HMO-II > Cu-doped goethite > Ni-doped goethite > Pb-doped goethite > pure goethite. The maximum adsorption capacities of HMO-III, HMO-II, Cu-doped goethite, Ni-doped goethite, Pb-doped goethite and pure goethite respectively, at pH-3 and 303K are 0.42, 0.35, 0.19, 0.17 and 0.13mmol/g.
8. Chromate adsorption by each solid sample is highly pH dependent and decrease with increasing pH. By increasing the pH from 3 to 7, the %adsorption decreases from 64 to 37% by pure goethite, from 82 to 43% by Pb-doped goethite, from 71 to 38% by Ni-doped goethite and from 84 to 52% by Cu-doped goethite.

9. Increase in temperature favor chromate adsorption by pure, Ni-doped goethite and the sample HMO-III, while in case of Pb and Cu-doped goethite chromate adsorption decreases with increasing temperature.

10. Langmuir equation is applicable to the sorption data. The values of Langmuir constants, $X_m$ and $K_b$, show that among all the goethite samples used in the present study, Cu-doped goethite is the best adsorbent having the highest values of these constants. High values of $X_m$ and $K_b$ shows the high monolayer capacity of this adsorbent and strong binding between the adsorbate and adsorbent.

11. The values of $\Delta H$ (isosteric heat of adsorption) are consistent with the effect of temperature on the adsorption of chromate by these samples, showing that the process of adsorption is endothermic in case of pure and Ni-doped goethite and sample HMO-III, while exothermic in case of Pb and Cu-doped goethite.

12. FTIR analysis of the solids after chromate adsorption show that at the lowest pH of 3, adsorption of chromate on the solid surfaces, takes place both through innersphere and outersphere complexation, while at higher pH values innersphere complexation is the dominant mechanism for chromate ions adsorption that replace the OH$^-$, CO$_3^{2-}$ and NO$_3^-$ from the surface of the metal-doped goethite.
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