SOLID PHASE EXTRACTION OF HEAVY METALS USING LOW COST SORBENTS

BY

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UNIVERSITY OF PESHAWAR
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Certified that Fazal Wahid S/O Kachkool Khan has carried out his research and experimental work on the topic entitled as “Solid Phase Extraction of Heavy Metals using Low Cost Sorbents” under our guidance and supervision. His research work is original and his dissertation is worthy of presentation to the University of Peshawar for the award of degree of Doctor of Philosophy in Inorganic Chemistry.

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In the Name of Allah,

The Most Merciful and Compassionate the Most Gracious and Beneficent whose help and guidance we always solicit at every step, at every moment.
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ABSTRACT

The aim of present work is to investigate the sorption capacity of *salvadora persica*, activated carbon, chitosan and chemically modified chitosan for heavy metals from dilute solutions. *Salvadora persica* was converted into powdered form and characterized by using Infrared spectroscopy. It has various organic compounds and these compounds contain sulphur, oxygen and nitrogen in their skeletons and behave superbly as coordinating ligands for cations present in the aqueous solution and hence causing effective sorption. Activated carbon was also prepared from *salvadora persica* under vacuum at 673 K with different soaking time. The prepared activated carbons were characterized using Surface Area Analyzer. Percentage yield of the prepared activated carbons in different heating times prior to washing was different. The activated carbon yields obtained at 673 K were 54.78 %, 52.27 % and 50.31 % at 30, 45 and 60 min heating time, respectively. The yield of activated carbons decreased as the heating duration increased. Surface area decreased from 375 to 27 m²/g. 4-Acryloylmopholine was reacted with chitosan to alter it chemically. The amended chitosan holds different binding sites (chelating centers) in the form of oxygen and nitrogen. Different techniques were applied to illustrate the amended chitosan. Activated carbons, powdered *salvadora persica*, chitosan and the chemically modified chitosan were used as sorbents for different cations (Cu²⁺, Cd²⁺, Pb²⁺ and Ni²⁺). Among these cations copper showed highest sorption ability as compared to other and the sorption properties were in agreement with that of the Langmuir model. The activated carbon prepared at 30 min heating time, showed maximum sorption capacities for cations due to its larger surface area. The Freundlich, Langmuir and Temkin models (both linear and non linear methods) were used to assess the experimental statistics. For activated carbon and powdered *salvadora persica*, lower errors were shown by type one (I) of the Langmuir model as compared to Freundlich and Temkin models, so it is the appropriate model to explain the sorption phenomenon. Among the linear forms of the Langmuir isotherms, low error values were given by type four (IV) than other linear forms of Langmuir and the Freundlich model but higher than that of Temkin model, which shows that Temkin model fits better to the experimental data of chemically modified chitosan.
NOMENCLATURE

\( n_i \) the number of moles of metal ions in the initial solution (mmol/dm\(^3\))

\( n_s \) the number of moles of metal ions after equilibrium (mmol/dm\(^3\))

\( m \) is the mass of the sorbent used in each sorption process

\( b \) the Langmuir constant related to the affinity of binding sites and sorption energy

\( k_1 \) rate constant of pseudo-first order kinetic model (min\(^{-1}\))

\( k_2 \) the rate constant of pseudo-second order kinetic model (g/mg min)

\( K_F \) Freundlich constant indicating adsorption capacity (mg/g)

\( n \) Freundlich constant indicating intensity

\( N_f \) amount of heavy metal ions adsorbed (mg/g or mol/g)

\( N_f^{\text{exp.}} \) the experimental value of adsorption capacity (mg/g)

\( N_s \) the maximum sorption capacity of metal ions (mg/g or mol/g)

\( C_s \) is the equilibrium concentration of metal ions (mmol/dm\(^3\))

\( N_f^{\text{cal}} \) calculated amount of heavy metal ions adsorbed (mg/g or mol/g)

\( N_f^t \) amount of metal ions adsorbed on adsorbent at time \( t \) (mg/g)

\( r \) correlation coefficient

\( t \) time (min)

\( \chi^2 \) chi-square

\( R^2 \) coefficient of determination

\( SE \) standard error

\( CH \) chitosan

\( CHAM \) chemically modified chitosan
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Chapter-1

INTRODUCTION

1.1 Chitin and chitosan

Chitin was first discovered by a French scientist while studying mushroom in 1811 AD and named this product as chitin fungine [1]. Later on, Odier isolated the same product in 1823 AD from cuticle of insects with hot potassium hydroxide solutions, and named it chitin. The term chitin is derived from the Greek word that means covering. Odier acknowledged the presence of chitin in crab sheath and suggested that it is the essential substance of the exoskeletons [2]. Children showed the presence of nitrogen in the structure of chitin in 1924 AD. Both, Odier and Children used hot concentrated potassium hydroxide solutions for purification of chitin [2]. It is believed that they have actually isolated chitosan instead of chitin. Because elemental analysis shows an empirical formula of approximately C_{11}H_{17}O_{7}N_{2} which is closer for the disaccharides repeat unit of chitosan (C_{12}H_{22}O_{8}N_{2}) than that of chitin (C_{16}H_{26}O_{10}N_{2}). However, Rouget recognized and reported chitosan, who treated chitin with boiling concentrated potassium hydroxide solution and named this product as modified chitin [3]. In 1894 Hoppe-Seyler extracted chitin from the shells of crabs, scorpions and spiders with concentrated potassium hydroxide solution at 180°C and named it ‘chitosan’ rather than ‘modified chitin’ which has the same nitrogen content as the original chitin [3].

Odier concluded that the structural materials in the exoskeletons of insects and plants are similar, so there was some confusion between cellulose, chitin and chitosan. Heyn, Van Iterson and co-workers obtained similarity in the X-ray diffraction patterns of chitin derived from crustacean, fungi and insects with same structural confirmation [4]. Later Heller obtained the identical IR spectra for chitin derived from insect and fungal source [5]. In 1934, the production of chitosan, chitosan films and fibers were patented. The modern research of chitin and chitosan can be considered to have begun in the early 1970s, when it was realized that chitin constitutes a significant waste in seafood related processes. In fact, in the last three decades, profitable utilization of chitosan improved considerably that can be confirmed from patent applications in
Japan, Europe, China, Korea and particularly in U.S [6]. Presently, chitin is largely used as a raw material for chitosan, whose application fields are pharmaceutical, agricultural, food industries, cosmetics, biomedical, biotechnological, water treatment, paper and textile industry [7].

1.1.1 Source of chitin and chitosan

Chitin is a polysaccharide and it is synthesized by a vast number of living organisms. The exoskeleton of various aquatic flora and fauna is made of chitin for example arthropods, fungi coelenterates and yeast [8]. Annually, roughly one hundred billion tons is formed [9]. The crustaceans’ shells such as shrimps, lobsters, krills, prawn and crabs are the main commercial source of chitin [10]. Due to variation in composition and structure in miscellaneous sources have different amount of chitin. The crustaceans’ shells contain 40-45 % of chitin while mollusks, squid pens contribute about 35% chitin of the dry weight [11, 12]. Arthropod shells (exoskeletons) have 20-25 % chitin on dry weight basis [13]. Though some fungi have chitosan and chitin in their cell walls and could be utilized as a resource, however, in actual practice, chitosan is produced from chitin through deacetylation [14]. Honeybee, brachiopod, ant, scorpion, cicada sloughs, spider bumblebee and cockroach are also important sources of chitin [15-19].
Table 1.1 Contents of chitin and calcium carbonate [10-19]

<table>
<thead>
<tr>
<th>Source</th>
<th>Chitin (%)</th>
<th>CaCO₃(%)</th>
</tr>
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<tbody>
<tr>
<td>Shrimp cuticle</td>
<td>30-40</td>
<td>20-30</td>
</tr>
<tr>
<td>Squid pen</td>
<td>20-40</td>
<td>Negligible</td>
</tr>
<tr>
<td>Krill cuticle</td>
<td>20-30</td>
<td>20-25</td>
</tr>
<tr>
<td>Crab cuticle</td>
<td>15-30</td>
<td>40-50</td>
</tr>
<tr>
<td>Fungi cell wall</td>
<td>10-25</td>
<td>Negligible</td>
</tr>
<tr>
<td>Insect cuticle</td>
<td>5-25</td>
<td>Negligible</td>
</tr>
<tr>
<td>Clam/oyster shell</td>
<td>3-6</td>
<td>85-90</td>
</tr>
</tbody>
</table>

1.1.2 Isolation of chitin and formation of chitosan

In animals, chitin is associated with residual proteins, residuals lipids, inorganic materials and the coloring substances [20]. The main sources for the production of chitin are the shells of crab, shrimp and prawn. Chitosan is prepared from the shields (covering) of crustaceans in four stages and these stages consist of removal of protein, removal of color, removal of minerals and removal of acetylene groups. Usually, demineralization is conducted prior to deproteinisation. But in some cases deproteinisation is carried out prior to demineralization. Acid and alkaline reagents are employed for the elimination of minerals and proteins, respectively [21]. The mineral and protein contents changes from species to species. Some species have greater contents of chitin while some have lesser quantities. Preparation conditions, strength of acid contact time and temperature also play an important role in chitosan extraction and are different for different species [22,23]. Demineralization is carried out with dilute hydrochloric acid (0.25M to 1M) at a temperature, ranging from 273 to 373K and the ratio of this solution to solid ranging from 15:1 to 40:1. The demineralization could be made in one step or may be repeated.
many times [24]. The inorganic material is calcium carbonate, during acid treatment calcium decomposes releasing carbon dioxide gas and calcium is removed as calcium chloride. The duration for demineralization is 6–15 h, depending on the species [25].

\[
\text{CaCO}_3 + \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

Deproteinization is usually carried out with alkaline treatment (1M NaOH) at a temperature ranging from 298 to 373 K for different period of time (1 to 36 h) with different ratio of solution to solid in a single treatment or may be repeated several times [26]. However, prolonged alkaline treatment and severe conditions may cause depolymerization and deacetylation [27].

The color pigments in chitin can be removed with organic solvent (hydrogen peroxide), ozone, potassium permanganate or bleaching agents [28]. Decolorized high molecular weight chitosan can also be obtained after deacetylation step by sun drying without using bleaching agent [29]. Chitosan is obtained by the removal of acetyl group from chitin with the help of basic solution. Extraction of chitosan from chitin could be done with NaOH or KOH solution but the commonly used reagent is sodium hydroxide solution and gives high molecular weight chitosan. In deacetylation, chitin is treated with 40–60% sodium hydroxide at a wide range of temperature (333K–423K) for different period of time, (1–36 h) in the presence of oxygen or inert conditions [30, 31].

Different researchers used different solution to solid ratio (10:1–30:1). The treatment time and temperature depends upon the concentration of solution, higher the concentration of alkaline solution used, lower will be the temperature and treatment time. However, the chitin undergoes degradation due to high concentration of solution, high temperature, and prolonged treatment during deacetylation [32, 33]. The deacetylation rate of chitin is usually determined by the extent of swelling of the chitin particles. A reaction time of 5 min with 45% NaOH may not be enough for chitin particles to be sufficiently swollen. Higher degree of deacetylation requires 40% alkali concentration and increased time of > 30 min [34].
1.1.3 Degree of Deacetylation

Elimination level of acetyl groups from chitin gives the quantity of free amino groups and differentiates between chitin and chitosan. Removal of acetyl groups from chitin up to 75% or above is generally known as chitosan and the properties and qualities of chitosan are mostly associated with the numbers of free amino groups [35]. During deacetylation process, difference in temperature and in strength of sodium hydroxide solution could enhance or reduce the removal of acetyl groups from chitin, producing chitosan with different properties [36]. Chitosan with different degree of deacetylation (DD) values have different ion-exchange capacity, solubility, viscosity and reaction with amino group [37]. Therefore, it is important to have a simpler, accurate and rapid method for the determination of the DD. Commercial chitosan usually has a deacetylation level from 70 to 95% and molecular mass (molar weight) from $10^4$–$10^6$gmol$^{-1}$ [38]. Different techniques have been applied to decide level of deacetylation of chitosan such as, potentiometric titration, conductometric titration, FTIR [39-46], acid-base titration method [47], colloidal titration method [48], first derivative UV spectrophotometry (1DUVS) [49], UV spectrophotometry [50], by a literature circular dichroism (c.d.) method, X-ray powder diffraction [51], and elemental analysis [52].

It is difficult to select a technique to for the grit of level of deacetylation of chitosan, however, nuclear magnetic resonance spectroscopy ($^1$H NMR) is one of the accurate and dependable technique.

1.1.4 Structure of chitin and chitosan

The structure of chitin is similar to that of cellulose but the only difference is the presence acetamido group on carbon-2 instead of hydroxyl group as shown in Fig 1.1. Chitin is a polysaccharide containing nitrogen. It is white, inelastic and hard [53]. Chitin is converted into chitosan by removal of acetyl group with the help of basic solution. It is α[(1→4)2-amino-2-deoxy-β-D-glucan] [54]. Chitin has three types, depending on the arrangement of molecules. These are known as alpha (α), beta (β) and gamma (γ) chitin as shown in fig.1.2-1.4 [55-56]. Chitin, in which the arrangement of molecules is opposite to each other known as alpha (α) chitin.
Alpha chitin forms strong hydrogen bonding (intermolecular) due to opposite arrangement of molecules. It is the firm structure as compare to other structures [57]. In beta (β) chitin, the monomeric molecules are arranged in the same direction and having weak hydrogen bond due to larger distances as compared with that of alpha chitin [58], but it is more reactive due to weak hydrogen bonding than alpha chitin [59]. Gamma (γ) type of chitin is an amalgamation of the other two types [60]. Interchain and intrachain hydrogen bonding are responsible for stable structures of chitin and chitosan [61-62].

Fig.1.1 Structures of Chitin, Chitosan and Cellulose
Fig. 1.2 Three polymorphic configurations of chitin: (a) α-chitin, (b) β-chitin, and (c) γ-chitin [57-60]

Fig. 1.3 Molecular structure and Hydrogen bonding in α-Chitin [61]
The importance of chitosan is recognized due to the presence of some reactive functional groups. These important and coordinating groups consist of one amino group and two hydroxyl groups. Amino group is the main distinction between chitin and chitosan [63-65].

Alpha (α) and beta (β) chitin cannot be dissolved in common solvents, but can only be dissolved in N-methyl-2-pyrrolidone and in a mixture lithium chloride and dimethylacetamide [66-67]. Chitosan has a basic nature and can be dissolved in acidic solution (aqueous) due to protonation of amino group [68-72].

Fig. 1.4 Molecular structure and Hydrogen bonding in β-Chitin
1.1.5 Interaction with metal ions

Chitosan has enormous chelating nature for cations due to its amino and hydroxyl groups [73]. It can bind cation in aqueous solution and its sorption abilities is attributed to the number of free amino groups in its structure [74-76], but pH of cation solution and properties of cation also affect sorption phenomenon [77-78]. Different coordinating mechanisms of chitosan with metal ions have been suggested which are given in Fig.1.5 - 1.9. Fig.1.5 - 1.7 suggest that amino groups from different chains, coordinating with metal cations via intra- or intermolecular complexation, Electron spin resonance (ESR) study suggests that in chitosan, Cu$^{2+}$ is coordinated with four nitrogen ligands in a square-planar geometry or tetrahedral distorted structure of two nitrogen and two oxygen ligands. [80-82].

Fig.1.5 proposed mechanisms of sorption of copper on chitosan [79-80]

Fig.1.6 Proposed mechanism for intermolecular complexes of chitosan with metal ions in a neutral or slightly cidic pH [81]
Paulino and his co-worker proposed that the complex between nickel ion and chitosan is formed due to the attachment of different amino groups from different polymer chain as shown in Fig.1.8. However, the interaction of nickel ion with the amino group of chitosan is weak in case of antiparallel molecular arrangement (α-chitosan). The sorption of Ni$^{2+}$ ion may be increased using β-chitosan, because the formation of the Chitosan-Ni complex is more suitable when the molecular arrangement is in parallel fashion [83].

Many authors suggested a different mechanism for the complex formation. They proposed that the complex is formed by amino groups and some hydroxyl groups (deprotonated) of chitosan. It
means that complex formed when hydrogen ions are released form chitosan groups [84,85], as shown in Fig.1.9.

![Proposed mechanism for the formation of complex between chitosan, Ni and Cu](image)

**Fig.1.9** Proposed mechanism for the formation of complex between chitosan, Ni and Cu

### 1.2 Phytoremediation

The process of utilizing living organisms such as plant, protozoa, bacteria, fungi, and algae to decrease or remove the harmful cations from the environment is called bioremediation. When plants or plant material are used for remediation then known as phytoremediation.

Certain plants have the abilities to remove and collect metals ions which played a vital role in the progress of phytoremediation method. The indispensable endeavor of research in this ground is to develop simple, easy, regenerative method to eliminate toxic cations from the surroundings [86].

The process through which plants are removing or reducing contaminants from the environment are given bellow:

#### 1.2.1 Phytoextraction

The removal of heavy metal ions and pollutants by plants from environment is called phyto extraction.
1.2.2 Phytotransformation
The degradation of intricate organic molecules with plant tissue is carried out in this process.

1.2.3 Phytostimulation
Plants secrete various enzymes and send these enzymes to their roots in this process and motivate microbes to degrade pollutants.

1.2.4 Phytostabilization
In this technique plants are used to decrease accessibility of cations into the environment and as a consequence their movement to water or foodstuff is prevented [87].

1.2.5 Phytovolatilisation
This is a method in which plants are used to volatilize pollutants [87].

1.2.6 Rhizo-filtration
In this technique plant roots are used to sorb organic and inorganic pollutants from water.

1.2.7 Pump and tree
The extracted pollutants are evaporated by plants in this process.

1.2.8 Hydraulic control
Suitable plant species are applied to maintain and control water table [88]. Plant wastes are applied to sorb toxic metal ions from solutions, plant material is more advantageous, as these are easily obtainable in huge amount and economical [89-90]. Different plant material are used to remove cations from water (waste water) such as papaya wood [91], maize leaf [92], leaf powder [93], rubber leaf powder [94.95], peanut hull pellets [96], sago waste [97], tree fern [98-100], rice husk ash and neem bark [101], grape stalk wastes [102], seaweed, mold, bacteria, and yeast [103-104]. The intention of the current work is to judge the sorption capacity of *salvadora persica* for heavy metals from dilute solutions (aqueous).

1.3 Activated carbon
Activated carbon, also known as activated charcoal is a form of carbon [105]. It is prepared from organic material under proper environment [106,107]. Activated carbons are highly porous material and only 1 g has a surface area of about 500 m² [107]. All carbon containing materials,
specially wood, coal and petroleum pitch materials, are used for the formation of activated carbon. It can be prepared by physical activation or chemical activation. In physical activation carbon content is heated in the presence of inert gases or in the presence of oxygen or under vacuum. In case of chemicals activation, H₃PO₄ and ZnCl₂ are extensively added for impregnation purposes, [108]. Zinc chloride produces activated carbon with higher degree of surface area than that of phosphoric acid [109]. However, phosphoric acid activation is widely favored over zinc chloride because ZnCl₂ causes environmental troubles and the activated carbon, activated with it, cannot be used as sorbent in the food and pharmaceutical industries [110]. Once the impregnation is carried out then at low temperatures, the matter is converted into activated form. Chemical activation is superior than physical because it needs less heat and can be prepared in short time. [111]. “Activated carbons are carbonaceous materials having large surface areas, high degree of porosity and various functional groups” [112]. That is why; it is applied as sorbent [113]. Activated carbon usually increases the cost of the treatment process. However, to minimize the cost of the treatment processes, cheaper raw materials are chosen to be transformed into activated carbon [114]. A variety of agricultural by-products and wastes are used as raw resources. These precursors consist of coconut shell and wood [115], olive stones [116,117], sugarcane bagasse [118], palm seed [119], apple pulp [120], rubber seeds [121] and agricultural byproducts [122-124].

1.3.1 Types of activated carbon
Activated carbons are complex in nature and difficult to categorize on certain parameters. However, these are classified into powder, granular and pellet, based on their particle sizes and shapes, and each one has its own specific applications. Powder activated carbon has size less than 100 μm and diameter between 15 and 25 μm. Powdered activated carbons are mainly applied to liquid phase sorption, flue gas treatment and wastewater treatment. Granulated activated carbon has a relatively larger particle size, between 0.5 to 4.0 mm, compared to powdered form of the activated carbon and used for water treatment. Pellets form of active carbon have cylindrical shaped and its diameter lie between 4 and 7 mm, while length ranges from 8-15 mm. Pellets activated carbon is mostly used for gaseous purification.
1.3.2 Structure of carbonaceous materials

Carbon can form different structures based on hybridization [125]. Diamonds has sp$^3$-hybridized form. Graphitic and aromatic structures are based on sp$^2$ orbitals, while alkynes have sp hybridization [126-127]. Compounds of carbon are divided into graphitic and non-graphitic compounds or carbon [125]. Graphitic carbons are 3-dimensional graphite [128]. Activated carbon has larger surface area, porous structure and physical strength [129], based on these unique properties it is one of the best choice for sorption process [130]. Activated carbon has three types of pores; micropores, having width < 20 Å, mesopores width between 20-500 Å) and macropores width > 500 Å) [131].

1.4 Sorption of Heavy metals

Metals are important for infrastructures, transportation and even in various daily goods and products such as electronic, battery and photographic films. Although it is beneficial to human beings but at the same time, heavy metal is a major class of water pollutants to the environment. The term "heavy metals" is used for those metals which have density more than 5.0g cm$^{-3}$ [137]. Though it is somewhat vague definition but this term is usually applied to elements like cadmium, chromium, mercury, cobalt, copper and nickel, causing environmental contamination. Metals can be harmful to human and environment due to their toxic nature. Metal ions effects can be divided into acute and chronic effects. The acute effect is usually a disturbance of the sensation and the temporary malfunction of the digestive systems. If high dose of a metal is taken, it can be fatal because heart diseases and damage of the nervous system are common chronic effects of heavy metals. Since heavy metals are non-degradable in the environment and their released to the environment keep accumulating in the food chain, which can cause long term damage to soil and aquatic life [138] and also heavy metal poisoning to human beings [139]. Historical records show that heavy metals have caused catastrophes like the mine tailing accident of Aznalcollar Spain [140], the mercury dumping in Minamata Bay, Japan [141] and arsenic poisoning of groundwater in Bangladesh [142] are a few examples of environmental disasters caused by deliberate or accidental release of heavy metals [143,144].

Metal pollutants can be classified as essential and nonessential elements [145]. Essential elements are present in biological fluids at trace concentrations less than 1 μg per gram of wet mass.
While excess of essential metals are hazardous. For example, an excess of copper in the body causes Wilson’s disease and infantile cirrhosis [148]. An excessive concentration of copper is responsible for gastrointestinal disorder [149].

Non-essential elements are pollutants with potential risks for living organism. These include lead, aluminum, cadmium and mercury, exposure to them is associated with recognizable toxicity [150-151]. They also displace vital nutritional minerals from their proper position in the body, as observed for lead or cadmium that have the ability to substitute calcium in an enzymatic reaction, affecting its action to a large extent [150]. Reactive radicals are produced by Lead and can harm cell, DNA and cell membranes [153], causes a broad range of physiological, biochemical and behavioral dysfunctions in animals and humans [150,154], including, the central nervous systems [155], the haemopoietic [156], cardiovascular systems [157], kidneys [158], liver [159]and male and female reproductive systems [160,161]. Damage and decreased intelligence can be caused by extremely low dose of lead [162]. Children are particularly vulnerable to lead poisoning [163,164].

Heavy metal ions are highly toxic environmental pollutants and the improvement of techniques for their exclusion from aquatic environments has, been a very active area of research [165]. The ordinary technologies for removing heavy metals from wastewater include chemical electro deposition, precipitation and adsorption processes [166]. However, among these techniques sorption is cheap, simple and efficient method for cations remediation from aqueous media. Sorption is a surface phenomenon, quite different from absorption and similar to surface tension. Sorption is an outcome of surface energy. This happens because the molecules of the surface are attracted only from below and from the sides, while in the interior, molecules experience forces of attraction from all sides. Hence, the molecules at the surface experience a net attraction downward and on account of the unbalanced forces, the surface of a liquid or solid is in a state of strain. This implies that the surface molecules have higher energy than those present inside and when the surface of liquid or solid attracts other molecules, this energy is reduced. The exact nature of attraction between the surface molecules and sorbate molecules depends on the species involved. Depending on the nature of attractive forces between the sorbate and sorbent, sorption can be classified as i) Physical sorption and ii) Chemical sorption.
In physical sorption, Vander Waals' forces of attraction are involved in sorption process. Since it could simply be desorbed by heating or lessening the external pressure of the sorbate (in case of gases). In case of chemisorption, the forces of attraction are chemical bonding are which are very strong comparatively. Sorption phenomenon is evaluated and explained with the help of different models, however the most commonly used isotherms are Freundlich, Temkin and Langmuir isotherms.

1.4.1 Sorption Isotherms

The concentration of sorbate and sorbent at equilibrium is the basic requirement to explain the sorption process and this relationship at a particular temperature and pH is called an isotherm. Isotherms explain the shifting of a substance (sorbate) from one phase i.e gas or liquid to another phase (solid) at a given temperature and pH [167,168]. A variety of sorption isothermal models have been developed to explain the sorption process, but not a single one is universally applicable because all of them are based on assumptions and may or may not be applicable in a particular sorption process. Among these models, Langmuir, Freundlich, and Temkin are widely used [169]. The amount of sorbate sorbed in an experiment (mmolg⁻¹) is calculated with the following Equation

\[ N_f = \frac{n_i - n_s}{m} \]

\( N_f \) represents the adsorbed concentration in term of moles. \( n_i \) is the initial and \( n_s \) is the final concentration after equilibrium. Where \( m \) is the weight of sorbent.

1.4.1.1 Langmuir isotherm

This isotherm is one of the commonly known and widely used model, developed by an American chemist Irving Langmuir in 1916. Initially, it was developed for gaseous sorption on solid surface but later on it was also used to explain sorption process between liquid and solid phases. This model assumes that: (i) sorbate has uniform (homogeneous) sites for sorbate sorption; (ii) a site can accommodate only one molecule, it means that once a site is occupied by one molecule then the other molecule will not be sorbed on the same site, (iii) all the sites of a sorbent are similar in structures and having the same energies (iv) sorbed molecules do not interact with each other on sorbent surface. This model is expressed in the following Eq.
\[ \frac{Cs}{Nf} = \frac{Cs}{Ns} + \frac{1}{Nsb} \]

Where \( N_f \) and \( Cs \) represent highest sorption ability and equilibrium concentration, \( Ns \) give highest sorption competence and \( b \) sorption energy.

### 1.4.1.2 Freundlich Isotherm model

Freundlich isotherm was developed by a German physicist Herbert Max Freundlich in 1906. This model is the earliest one that explains the sorption equilibrium and sorption process. It assumes that: (i) sorbate has heterogeneous sites for sorbate sorption i.e, all site are different from one another in a given sorbate; (ii) It is not necessary that a site can accommodate only one molecule it means that once a site is occupied by one molecule then the other molecule will be sorbed on the same site, indicating multilayer sorption; (iii) all the sites of a sorbent are not similar in structures and having different binding energies, sites of stronger binding energies will be occupied first by sorbate molecules followed by the occupation of those sites having lesser binding energies [170-172]. Freundlich model is presently utilized in heterogeneous system of sorption process, slope of this model has a value between zero and one (0 – 1), indicating a measure of heterogeneity or sorption intensity. If the value approaches zero, it means that the surface is more heterogeneous [173]. The Freundlich isotherm is represented by the Eq. given bellow.

\[ Nf = K_F Cs \frac{1}{n} \]

\[ \log Nf = \log K_F + \frac{1}{n} \log Cs \]

Where \( K_F \) and \( n \) are constants, showing sorption capacity and sorption intensity of sorbent. The plot of \( \log N_f \) versus \( \log Cs \) for the sorption is used to generate \( K_F \) and \( n \) from the intercept and the slope values, respectively.
1.4.1.3 Temkin isotherm model

Temkin isotherm model was designed and presented by Temkin and Pyhez in 1940. The basic aim was to explain sorption of hydrogen on platinium electrodes in acidic medium. Main objective of the Temkin model is the consideration of interaction between sorbate and sorbent molecules, provided that the concentration will be neither very high nor very low. According to this model energy (heat) decreases as the surface occupation of the sorbent is increased due to sorbent-sorbate interaction. Temkin model also suggests that all binding sites on a given sorbent have uniform energies [174,175]. The mathematical forms of this model are given as:

\[ N_f = \ln(K_T C_s)^{\frac{1}{n_T}} \]

\[ N_f = n_T \ln K_T + n_T \ln C_s \]

A plot of \( \ln C_s \) versus \( N_f \) gives us \( K_T \), \( n_T \) and \( b \) values. The constant \( b \) is heat of sorption, and can be calculated from the following equation:

\[ n_T = \frac{RT}{b} \]

1.4.2 Linear Method

In this method all the isotherms are converted into their respective linear forms and then these linear forms of all isotherms are applied to a sorption experimental process. Parameters of each isotherm are calculated and then error functions are compared and the model which gives least error is selected to be suitable to explain the investigated data. It is important to note that during linearization into different linear forms, the error values are also changed and as a result different results will be obtained which helps in deciding the best fit model to the experimental data. Temkin and Freundlich and other isotherms are transformed into their linear forms and all of them have only one linear form, but Langmuir isotherm can be converted into four different linear forms.
1.4.3 Nonlinear Method

Linear forms of the different isotherms and even of the same isotherm, such as in case of Langmuir isotherm which have four different linerized forms, have different error values due to difference in their axial arrangements, so it is necessary to apply nonlinear regression method which is free from such axial arrangement errors. The resulted parameters from linear as well as nonlinear regression methods are compared and that linear form is selected which has closest possible values with nonlinear form of its own model and in this way the optimization is made and the best fitted isotherm is found which explain the sorption process.

1.4.4 Error Functions

Error function analysis is the application of mathematical techniques for sorption equilibrium to find the suitable isotherm for the experimental data, among the various error functions, the coefficient of determination ($R^2$), is the most important one and often used to predict the suitable model which can explain sorption studies. The best fit model is determined on the bases of magnitude of coefficient of determination ($R^2$), the model resulting in a value close to unity for coefficient of determination is considered the best fitted one [176-179]. The other error “functions such as sum of the square error, hybrid fractional error function and sum of absolute errors” [80]. In sorption studies, all the error functions or some of them are applied to find the isotherm model which comparatively well fit to the data. Error functions are detrimental in finding the suitable isotherm because error functions, having low value for a given isotherm, confirms that it is a suitable isotherm for the experimental data.

1.4.4.1 Sum of the Squares of the Errors (SSE)

Sum of the square of the errors (SSE) “is the most widely used error function and is defined as the sum of the squares of the difference between the data obtained by calculating from the isotherm models and the experimental data” [181]. It is expressed as

$$SE = \sqrt{\frac{1}{m-P} \sum_{i=1}^{m} (N_{\text{exp},i} - N_{\text{cal},i})^2}$$
1.4.4.2 Chi-Square Test ($\chi^2$)

“The Chi-Square is the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models” [182]. “The Chi-Square ($\chi^2$) will be very less if the experimental data and data from the model are similar and vice versa. Therefore, the isotherm model that gives the smallest chi-square value is considered the best-fit isotherm” [181].

\[
\chi^2 = \sum_{i=1}^{m} \frac{(N_{f \text{ exp } i} - N_{f \text{ cali } i})^2}{N_{f \text{ cali } i}}
\]

Where $N_{f \text{ exp }}$ is the number moles sorbed experimentally while $N_{f \text{ cali }}$ is the calculated number of moles from each model. The number of points present in each isotherm is $m$ and $P$ is the number of parameters in each equation.
Chapter-2

EXPERIMENTAL

2.1 Material
Roots of Salvadora persica roots were collected from a shop in pepalmandi, Peshawar. Chitosan having 78 percent level of deacetylation, (Norway) Hydrochloric acid (Merk), sodium hydroxide (Merk), lead nitrate (Merk), ortho phosphoric acid (Merk), cadmium nitrate, (Merck) nickel nitrate (Merk) and copper nitrate (Merk), acryloylmorpholine (Aldrich) and ethanol (Synth), were all of analytical grade and were used without purification.

2.2 Preparations

2.2.1 Preparation of sorbent from Salvadora persica
The collected roots of salvadora persica were cleaned. Then dried at a temperature 378 K in an oven for four hours (4 h). The desiccated roots were converted into powder form with the help of a grinder.

2.2.2 Preparation of activated carbon
Salvadora persica powder form was used for the preparation of activated carbon. Powdered salvadora was impregnated with ortho phosphoric acid solution (10 % (v/v)). During impregnation process 10 g of sample was added to 100 cm$^3$ of solution. The contact time for impregnation was 14 h. The impregnated powder was added to distilled water and filtered, this addition and filtration practice was repeated several times in order to get neutral pH. Then dried for 8 h in oven at 478 K. Tube furnace was used for the carbonization purposes. The sample was heated at 673 K under vacuum. The activated carbon produced from salvadora powder had different soaking times. The heating durations were 30, 45 and 60 min. The temperature of the products was brought to room temperature in vacuum and shifted to desiccators for further use.
2.2.3 Synthesis of chemically modified chitosan

Three gram (3g) of chitosan were added to a beaker containing 100 cm$^3$ of ethanol. This mixture was stirred for 20 min at a temperature of 328 K. Then 3 cm$^3$ of 4-acryloylmorpholine were also transferred to the beaker containing chitosan and ethanol. Triethyamine was used as a catalyst and only 1 cm$^3$ of the catalyst was added to the reaction mixture. Then stirred for 24 h at 328 K. The filtered product was washed, with ethanol. the modified chitosan was dried for six hours (6 h) under vacuum at 318 K. The proposed mechanism of reaction is shown in Fig. 2.1.

![Proposed Mechanism for synthesis of modified Chitosan](image)

**Fig.2.1** Proposed Mechanism for synthesis of modified Chitosan
2.3 Sorption experiments

Sorption capacities of chitosan, chemically modified chitosan, powdered *salvadora persica* and activated carbon were studied. About 20 mg of each sorbent was transferred separately into bottles (polyethylene). 25.0 cm$^3$ of sorbate solution was added to each bottle, different solutions of each sorbate have different concentrations ($7.0 \times 10^{-4}$ to $2.0 \times 10^{-3}$ mol dm$^{-3}$). In order to determine the required time for sorption saturation, sorption of the cations were noted at different interval of time at 298 K and it was found that sorption equilibrium occurs after 4 h. But 6 h were selected as contact time in order to have satisfactory equilibrium environment as shown in fig. 2.2. Suitable pH is very important because it affect the sorption capacity. In order to have appropriate pH for sorption, Experiments for sorption were carried out in different pH environments, ranging from pH 2 to 6. At higher pH (more than 6) lead, nickle and copper ions become insoluble due to formation of hydroxides [181,182]. At low pH The sorption capacity of ions were due to the presence of more hydrogen ions in the solution. Because hydrogen ion compete with metal ions for active sites. At pH 5.6 copper, lead and nickel ions showed maximum sorption and chosen as optimum pH in the present study. The left over concentration of cations after equilibrium was established by means of atomic absorption spectrophotometer.

![Fig.2.2 Effect of Contact time on sorption of copper onto Salvadora persica](image-url)
Chapter-3

RESULTS & DISCUSSION

3.1 Infrared spectra of *Salvadora persica* roots

The FTIR spectrum of the *salvadorapersica* shows absorption bands at 3298, 1049, 1018, 1049, 1627 1430, 1558 and 1257 cm\(^{-1}\) indicating the presence of OH and amino group, bridged C−O−C, hemicelluloses, cellulose, C=C, CH\(_3\) [183], C=O of amide group [184] and C−O−C in the cellulose chain and OH deformation respectively as shown in Figure 3.1.

![Infrared spectrum of *Salvadora persica*.](image)
3.2 Sorption study of powdered roots of *salvadora persica*

*Salvadora persica* has various organic compounds and these compounds contain sulphur, oxygen and nitrogen in their skeletons and behave superbly as coordinating ligands for cations present in the aqueous solution and hence causing effective sorption. $N_f$ represents the amount of sorbate adsorbed while $N_s$ the highest sorption capacity of sorbate and $b$ is the interaction energy. These values are summarized in Table 3.1. The results indicated that salvadora persica has better sorption power for copper, lead and nickel (Cu$^{2+}$, Pb$^{2+}$ and Ni$^{2+}$) and its order of cations sorption is Cu$^{2+}$ > Ni$^{2+}$ > Pb$^{2+}$ as shown in Fig. 3.2 and 3.3.
Table 3.1. Number of moles sorbed \((N_f)\), Langmuir parameters \((N_s\) and \(b)\), coefficient of determination \((R^2)\) and standard error \((SE)\) for the interaction of divalent metals with *salvadora persica* at 298 ± 1 K, using different linear form of Langmuir isotherm.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Parameters</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
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<tr>
<td></td>
<td>(N_f) (mmol g(^{-1}))</td>
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<td>1.75</td>
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<tr>
<td>Cu(^{2+})</td>
<td>(N_s) (mmol g(^{-1}))</td>
<td>1.84±0.18</td>
<td>1.93±0.51</td>
<td>1.92±1.92</td>
<td>1.93±4.37</td>
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<td>(b) (g mmol(^{-1}))</td>
<td>2.94±0.54</td>
<td>2.26±0.22</td>
<td>2.32±0.43</td>
<td>2.26±2.26</td>
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<td></td>
<td>(R^2)</td>
<td>0.998</td>
<td>0.991</td>
<td>0.971</td>
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<td></td>
<td>SE</td>
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<td></td>
<td>(\chi^2)</td>
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<td>Pb(^{2+})</td>
<td>(N_f) (mmol g(^{-1}))</td>
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<td></td>
<td>(N_s) (mmol g(^{-1}))</td>
<td>1.01±0.81</td>
<td>1.13±0.87</td>
<td>1.08±1.08</td>
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<td>(b) (g mmol(^{-1}))</td>
<td>1.21±0.98</td>
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<tr>
<td>Ni(^{2+})</td>
<td>(N_f) (mmol g(^{-1}))</td>
<td>1.53</td>
<td>1.53</td>
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<td></td>
<td>(N_s) (mmol g(^{-1}))</td>
<td>2.42±1.62</td>
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<td></td>
<td>(b) (g mmol(^{-1}))</td>
<td>0.25±0.41</td>
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</table>
Fig. 3.2 Experimental sorption isotherm for nickel (●) and copper (■) on *salvadora.persica*.

Fig. 3.3 Experimental sorption isotherm for lead (■) on *salvadora persica*.
The Langmuir, Freundlich and Temkin are the famous models and used in the sorption study. Linear forms of these models are shown in Fig. 3.4.

The Langmuir isotherms transformed into four different linear forms and all of which were applied to the sorption study. The parameters of these equations and equilibrium models often lead us to understand the mechanisms of sorption, surface properties and affinity of the sorbent. The calculated values of Langmuir, Freundlich and Temkin isotherms for nickel are shown in Fig.3.5

![Fig.3.4 Linear Langmuir sorption isotherm for copper (■), lead (▲) and nickel (●) on salvadora](image-url)
Both linear and non-linear regression analysis were used to evaluate sorption process for better results. The Langmuir, Freundlich and Temkin isotherms obtained, using non-linear regression techniques for sorption of copper, lead and cadmium onto *Salvadora Persica* are shown in Figures 3.6-3.8.
Fig. 3.6 Nonlinear Langmuir (●), Temkin (○), Freundlich (▼) and experimental sorption isotherms (■) for copper on *salvadora*.

Fig. 3.7 Nonlinear Langmuir (●), Temkin (○), Freundlich (▼) and experimental sorption isotherms (■) for lead on *salvadora*.
Table 3.2 shows that the values of $R^2$ for Freundlich and Temkin are smaller than that of the Langmuir isotherm of type 1. The values of Error functions (SE and chi-square ($\chi^2$)) are lowest for the Langmuir (I) than for other three types as well as from Freundlich. It means that Langmuir (I) is in agreement with the experimental data.
Table 3.2. Number of moles sorbed ($N_f$), the Freundlich ($n$ and $K_f$), the Temkin ($b$ and $K_T$) parameters, coefficient of determination ($R^2$) and the respective error for interaction of divalent metals with *salvadora persica* at 298 ± 1 K, using linear method.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Pb$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>0.52±0.28</td>
<td>1.26±0.10</td>
<td>0.48±0.31</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>2.58±0.38</td>
<td>4.61±0.21</td>
<td>1.57±0.63</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.885</td>
<td>0.832</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>1.34</td>
<td>1.14</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.96</td>
<td>0.56</td>
<td>0.27</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>10.24±0.54</td>
<td>86.53±1.30</td>
<td>2.49±0.59</td>
</tr>
<tr>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>0.578±0.23</td>
<td>0.723±0.29</td>
<td>1.33.46±0.53</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.923</td>
<td>0.879</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>0.08</td>
<td>0.68</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The isothermal parameters of the three models were also determined by using non-linear regression analysis. It is to be noted that the values of constants of the Langmuir isotherm, determined by this method, are very close to the results of the Langmuir model Type 1. However, the values of different error functions corresponding to the non-linear Langmuir equation are smaller than those of the Freundlich and the Temkin models as shown in Table 3.3.
Table 3.3. Number of moles sorbed (Nf), the Freundlich (n and Kf), Temkin (K_T and b) parameters, coefficient of determination (R^2) and respective error for interaction of Cu^{2+}, Pb^{2+} and Ni^{2+} with *salvadora persica* at 298 ± 1 K, using non-linear method.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Cu^{2+}</th>
<th>Pb^{2+}</th>
<th>Ni^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Nf (mmol g^(-1))</td>
<td>1.75</td>
<td>0.84</td>
<td>1.53</td>
</tr>
<tr>
<td></td>
<td>Ns (mmol g^(-1))</td>
<td>1.90±0.03</td>
<td>1.05±0.04</td>
<td>2.31±0.16</td>
</tr>
<tr>
<td></td>
<td>b (g mmol^(-1))</td>
<td>2.41±0.18</td>
<td>1.08±0.14</td>
<td>0.28±0.04</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.980</td>
<td>0.966</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>χ^2</td>
<td>0.002</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>Freundlich</td>
<td>K_f (mmol g^(-1))</td>
<td>1.29±0.05</td>
<td>0.54±0.02</td>
<td>0.55±0.05</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>5.41±0.89</td>
<td>3.02±0.46</td>
<td>1.92±0.22</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.834</td>
<td>0.875</td>
<td>0.928</td>
</tr>
<tr>
<td></td>
<td>χ^2</td>
<td>0.018</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Temkin</td>
<td>K_T (mmol dm^(-3))</td>
<td>91.04±58.82</td>
<td>10.29±3.03</td>
<td>2.53±0.30</td>
</tr>
<tr>
<td></td>
<td>b (kJ mol^(-1))</td>
<td>0.716±0.43</td>
<td>0.723±0.43</td>
<td>1.34±0.11</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.888</td>
<td>0.932</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td>χ^2</td>
<td>0.012</td>
<td>0.002</td>
<td>0.006</td>
</tr>
</tbody>
</table>

The non-linear regression analysis corresponds to the best way to select the isotherm that fits the experimental data. This method involves an attempt to minimize the distribution of errors between experimental data and the isotherm considered [185]. Both linear and non-linear regression analysis produce different models as the best fitting isotherm for the given set of data, thus indicating a significant difference between the analytical methods.

3.3 Activated carbon

Percentage yield of the prepared activated carbons in different heating times prior to washing was different. The activated carbons yield obtained at 673 K were 54.78 %, 52.27 % and 50.31 % at 30, 45 and 60 min heating time respectively. The yield of activated carbons decreased as the heating duration increased. As the duration of carbonization increases from 30 min to 60 min at
673 K, resulted a decrease in surface area (375 - 27 m²/g). Because pores become larger at added heating time and then collapse (Table 3.4) [186].

**Table 3.4. Porosity of activated carbon as determined by nitrogen adsorption**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>375</td>
<td>1.21</td>
<td>128.97</td>
</tr>
<tr>
<td>45</td>
<td>221.54</td>
<td>0.67</td>
<td>123.5</td>
</tr>
<tr>
<td>60</td>
<td>27.07</td>
<td>0.03</td>
<td>35.32</td>
</tr>
</tbody>
</table>

The use of phosphoric acid during activation promotes depolymerization, dehydration, and redistribution of constituent biopolymers and also favoring the conversion of aliphatic to aromatic compounds [187].

### 3.4 Sorption study

Activated carbon, thus prepared was applied to study the sorption process of divalent cations of lead, copper and nickel from aqueous solutions. The quantity of cations sorbed $N_f$, the maximum sorption capacity $N_s$, the interaction energy $b$ and the correlation coefficient ($r$) obtained from the linearized form of the Langmuir model are given in Tables 3.5a - c.
Table 3.5a. Number of moles sorbed ($N_f$), Langmuir parameters ($N_s$ and $b$), correlation coefficient determination ($R^2$) and standard error (SE) for the interaction of divalent metals with activated carbon (prepared at 673 k for 30 min at 298 ± 1 K, using different linear form of Langmuir isotherm minutes).

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Metal ions</th>
<th>Parameter Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>1.17</td>
<td>1.17</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.22±0.21</td>
<td>1.31±0.26</td>
<td>1.30±1.30</td>
<td>1.31±3.52</td>
</tr>
<tr>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>3.71±0.81</td>
<td>2.69±0.28</td>
<td>2.76±0.36</td>
<td>2.67±2.67</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.996</td>
<td>0.996</td>
<td>0.964</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>0.03</td>
<td>0.053</td>
<td>0.052</td>
<td>0.061</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.009</td>
<td>0.017</td>
<td>0.017</td>
<td>0.018</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>1.01</td>
<td>1.01</td>
<td>1.01</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.13±0.50</td>
<td>1.43±0.69</td>
<td>1.24±1.24</td>
<td>1.35±1.39</td>
</tr>
<tr>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.73±0.88</td>
<td>0.92±0.75</td>
<td>1.25±0.79</td>
<td>1.03±1.03</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.989</td>
<td>0.973</td>
<td>0.798</td>
<td>0.798</td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>0.06</td>
<td>0.11</td>
<td>0.070</td>
<td>0.093</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.037</td>
<td>0.10</td>
<td>0.047</td>
<td>0.081</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.01±0.61</td>
<td>1.05±0.94</td>
<td>1.05±1.05</td>
<td>1.06±1.44</td>
</tr>
<tr>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.60±0.98</td>
<td>1.39±0.68</td>
<td>1.38±0.72</td>
<td>1.35±1.35</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.991</td>
<td>0.972</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td>SE</td>
<td>0.018</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.001</td>
<td>0.008</td>
<td>0.008</td>
<td>0.008</td>
</tr>
</tbody>
</table>
Table 3.5b. Number of moles sorbed ($N_f$), Langmuir parameters ($N_s$ and $b$), coefficient of determination ($R^2$) and standard error (SE) for the interaction of divalent metals with activated carbon (prepared at 673 K for 45 min) at 298 ± 1 K, using different linear form of Langmuir isotherm.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Metal ions</th>
<th>Parameter Type</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>Cu$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.08±0.58</td>
<td>1.29±0.07</td>
<td>1.17±0.09</td>
<td>1.30±1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.58±0.91</td>
<td>0.94±0.07</td>
<td>1.24±0.17</td>
<td>0.94±0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.983</td>
<td>0.930</td>
<td>0.721</td>
<td>0.721</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.055</td>
<td>0.08</td>
<td>0.65</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.048</td>
<td>0.05</td>
<td>0.075</td>
<td>0.050</td>
</tr>
<tr>
<td>45</td>
<td>Pb$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>0.96±0.89</td>
<td>1.05±0.03</td>
<td>1.02±0.03</td>
<td>1.04±0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.15±1.03</td>
<td>0.90±0.04</td>
<td>0.98±0.09</td>
<td>0.92±0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.991</td>
<td>0.986</td>
<td>0.933</td>
<td>0.933</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.019</td>
<td>0.021</td>
<td>0.026</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.001</td>
<td>0.007</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>45</td>
<td>Ni$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>0.90±0.08</td>
<td>0.97±0.02</td>
<td>0.95±0.02</td>
<td>0.96±0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.91±0.01</td>
<td>1.36±0.01</td>
<td>1.46±0.04</td>
<td>1.41±0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.996</td>
<td>0.964</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.035</td>
<td>0.027</td>
<td>0.031</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.009</td>
<td>0.010</td>
<td>0.012</td>
<td>0.015</td>
</tr>
</tbody>
</table>
Table 3.5c. Number of moles sorbed ($N_f$), Langmuir parameters ($N_s$ and $b$), coefficient of determination ($R^2$) and standard error (SE) for the interaction of divalent metals with activated carbon (prepared at 673 K for 60 min) at 298 ± 1 K, using different linear form of Langmuir isotherm

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Metal ions</th>
<th>Parameter</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Cu$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>0.87±0.06</td>
<td>0.93±0.02</td>
<td>0.93±0.93</td>
<td>1.31±2.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>3.71±0.02</td>
<td>2.69±0.007</td>
<td>2.76±0.36</td>
<td>2.67±2.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.996</td>
<td>0.996</td>
<td>0.964</td>
<td>0.964</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.027</td>
<td>0.033</td>
<td>0.035</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.08</td>
<td>0.011</td>
<td>0.012</td>
<td>0.13</td>
</tr>
<tr>
<td>60</td>
<td>Pb$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>0.69±0.13</td>
<td>0.85±0.13</td>
<td>0.56±0.12</td>
<td>0.84±0.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>2.25±0.04</td>
<td>1.15±0.11</td>
<td>1.75±0.12</td>
<td>1.20±0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.990</td>
<td>0.881</td>
<td>0.647</td>
<td>0.647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.05</td>
<td>0.069</td>
<td>0.055</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.03</td>
<td>0.058</td>
<td>0.042</td>
<td>0.05</td>
</tr>
<tr>
<td>60</td>
<td>Ni$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>0.58±0.07</td>
<td>0.64±0.12</td>
<td>0.61±0.03</td>
<td>0.64±0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>5.04±0.03</td>
<td>3.17±0.07</td>
<td>3.87±0.05</td>
<td>3.09±0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.866</td>
<td>0.756</td>
<td>0.756</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.031</td>
<td>0.034</td>
<td>0.033</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.010</td>
<td>0.014</td>
<td>0.011</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Experimental and linear form of Langmuir sorption isotherm for nickel on activated carbon prepared at 30 min heating time (Fig. 3.9). Activated carbon prepared at different heating time showed different sorption capacity. Activated Carbon prepared at 30 minutes heating time
showed greater sorption capacity for Cu\(^{2+}\), Pb\(^{2+}\) and Ni\(^{2+}\) and its order of cations sorption is Cu\(^{2+}\) > Pb\(^{2+}\) > Ni\(^{2+}\). Increase in time for the preparation of activated carbon gives smaller surface area and hence, causes decrease in sorption capacity of cations.

The Langmuir, Freundlich and Temkin models are the three most common isothermal models that are used to describe these systems in equilibrium at solid/liquid interface. The Langmuir

**Fig. 3.9** Experimental sorption isotherm of activated carbon prepared at 673 K for (a) 30 (b) 45, and (c) 60 minutes. The line with points (●), (■), and (▲) represents lead, copper, and nickel, respectively.
isotherm can be transformed to at least four linear forms and all of which are applied to this sorption study. The parameters of these equations and equilibrium models often lead us to understand the mechanisms of sorption, surface properties and affinity of the sorbent. Both linear and non-linear regression analysis were used to evaluate sorption process to ensure better results. It was observed that the predicted values of constant and the correlation coefficients values for all four linear forms of the Langmuir isotherms are quite different (Table 3.5a-3.5c). The value of correlation coefficient obtained from the Langmuir isotherm, type 1, is greater than the other three linear equations. It suggests that the Langmuir type 1 fits better to the experimental data in comparison with the other linear forms of the Langmuir isotherm. Error functions, SE and chi-square $\chi^2$ showed minimum values for the Langmuir model type 1, than other three types of the Langmuir equations which suggest that Langmuir model type 1 fits better to the experimental data for sorption on activated carbons prepared at different heating time. The excellent fitness of the Langmuir isotherm type 1 to the experimental data confirms that the sorption occurs in monolayer, each molecule has the same activation energy and the interaction sorbate/sorbate is negligible. The error functions for the Freundlich isotherms showed higher values than the Langmuir isotherm of type 1, (Table 3.5a-3.5c). For all the material, but gave lower values for the Temkin model Table 3.6(3.6a &3.6b), as compared to the other three forms of linear Langmuir isotherms.
Table 3.6a Number of moles sorbed ($N_f$), the Freundlich ($n$ and $K_f$), the Temkin ($b$ and $K_T$) parameters, coefficient of determination ($R^2$) ($r$), and the respective error for interaction of divalent metals with activated carbon (prepared at 673 K for 30 and 45 min) at 298 ± 1 K, using linear method.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Isotherm</th>
<th>parameters</th>
<th>Pb$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>0.62±0.20</td>
<td>0.81±0.08</td>
<td>0.54±0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>2.60±0.38</td>
<td>3.09±0.32</td>
<td>2.93±0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.798</td>
<td>0.847</td>
<td>0.893</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$SE$</td>
<td>1.32</td>
<td>1.24</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.97</td>
<td>0.85</td>
<td>1.23</td>
</tr>
<tr>
<td>30</td>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>16.07±0.68</td>
<td>45.09±0.88</td>
<td>17.94±0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>612.65±0.24</td>
<td>575.94±0.23</td>
<td>508.01±0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.864</td>
<td>0.910</td>
<td>0.944</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$SE$</td>
<td>0.10</td>
<td>0.09</td>
<td>0.057</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.09</td>
<td>0.075</td>
<td>0.036</td>
</tr>
<tr>
<td></td>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>0.49±0.30</td>
<td>0.62±0.20</td>
<td>0.50±0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>2.72±0.36</td>
<td>2.97±0.36</td>
<td>3.09±0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.898</td>
<td>0.780</td>
<td>0.833</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$SE$</td>
<td>1.45</td>
<td>1.26</td>
<td>2.86</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.76</td>
<td>0.76</td>
<td>1.32</td>
</tr>
<tr>
<td>45</td>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>10.39±0.01</td>
<td>15.24±0.64</td>
<td>24.64±0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>0.54±0.02</td>
<td>0.590±0.23</td>
<td>0.42±0.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.935</td>
<td>0.817</td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$SE$</td>
<td>0.039</td>
<td>0.082</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.010</td>
<td>0.062</td>
<td>0.051</td>
</tr>
</tbody>
</table>
Table 3.6b Number of moles sorbed ($N_f$), the Freundlich ($n$ and $K_f$), the Temkin ($b$ and $K_T$) parameters, coefficient of determination ($R^2$), and the respective error for interaction of divalent metals with activated carbon (prepared at 673 K for 60 min) at 298 ± 1 K, using linear method.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Isotherm</th>
<th>parameters</th>
<th>Pb(II)</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>0.96±0.02</td>
<td>0.816±0.02</td>
<td>1.06±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>3.32±0.05</td>
<td>3.09±0.04</td>
<td>2.80±0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.715</td>
<td>0.847</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>7.13</td>
<td>1.9</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>3.27</td>
<td>0.78</td>
<td>1.01</td>
</tr>
<tr>
<td>60</td>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>28.34±0.02</td>
<td>45.07±0.02</td>
<td>189.65±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>0.752±0.02</td>
<td>0.575±0.01</td>
<td>0.221±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.779</td>
<td>0.910</td>
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<td></td>
<td>SE</td>
<td>0.70</td>
<td>0.68</td>
<td>0.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.32</td>
<td>0.59</td>
<td>0.024</td>
</tr>
</tbody>
</table>

When the error value functions of the other three linear forms of the Langmuir isotherm are compared with the Freundlich, it is less appropriate to describe the sorption system than the other three models of the Langmuir (Figure 3.10). The isothermal parameters of the three models were also determined by using non-linear regression analysis. It is to be noted that the values of constants of the Langmuir isotherm as determined by this method, are very close to the results of the Langmuir model Type 1. However, the values of different error functions corresponding to the non-linear Langmuir equation are smaller than those of the Freundlich and the Temkin models Table 3.7(a & b) and Figure 3.11. The non-linear regression analysis corresponds in the best way to select the isotherm that fits the experimental data. This method involves an attempt to minimize the distribution of errors between experimental data and the isotherm considered [188]. Both linear and non-linear regression analysis produce different models as the best fitting
isotherm for the given set of data, thus indicating a significant difference between the analytical methods.

**Table 3.7a** Number of moles sorbed ($N_f$), the Freundlich ($n$ and $K_f$), Temkin ($K_T$ and $b$) parameters, coefficient of determination ($R^2$) and respective error for interaction of Cu$^{2+}$, Pb$^{2+}$ and Ni$^{2+}$ with activated carbon (prepared at 673 K for 30min) at 298 ± 1 K, using non-linear method.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Isotherm</th>
<th>parameters</th>
<th>Cu$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Langmuir</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>1.17</td>
<td>1.01</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.28±0.03</td>
<td>1.20±0.05</td>
<td>1.05±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>2.94±0.32</td>
<td>1.47±0.24</td>
<td>1.43±0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.979</td>
<td>0.942</td>
<td>0.988</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.002</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>30</td>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>0.84±0.04</td>
<td>0.67±0.04</td>
<td>0.57±0.03</td>
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<tr>
<td></td>
<td></td>
<td>$n$</td>
<td>3.98±0.71</td>
<td>3.39±0.63</td>
<td>3.53±0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.847</td>
<td>0.800</td>
<td>0.887</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\chi^2$</td>
<td>0.019</td>
<td>0.016</td>
<td>0.007</td>
</tr>
<tr>
<td>30</td>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>45.09±19.62</td>
<td>15.43±5.94</td>
<td>18.01±4.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>4.30±0.47</td>
<td>3.98±0.48</td>
<td>4.88±0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.921</td>
<td>0.884</td>
<td>0.949</td>
</tr>
<tr>
<td></td>
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<td>$\chi^2$</td>
<td>0.009</td>
<td>0.009</td>
<td>0.005</td>
</tr>
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</table>
Table 3.7b. Number of moles sorbed (Nf), the Freundlich (n and Kf), Temkin (KT and b) parameters, coefficient of determination (R^2) and respective error for interaction of Cu^{2+}, Pb^{2+} and Ni^{2+} with activated carbon (prepared at 673 K for 45, and 60 min) at 298 ± 1 K, using non-linear m

<table>
<thead>
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<th>Time (min)</th>
<th>Isotherm</th>
<th>parameters</th>
<th>Cu^{2+}</th>
<th>Pb^{2+}</th>
<th>Ni^{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>Freundlich</td>
<td>Kf (mmol g⁻¹)</td>
<td>0.65±0.04</td>
<td>0.51±0.02</td>
<td>0.54±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>3.52±0.74</td>
<td>3.08±0.41</td>
<td>4.10±0.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R^2</td>
<td>0.780</td>
<td>0.896</td>
<td>0.837</td>
</tr>
<tr>
<td></td>
<td></td>
<td>χ^2</td>
<td>0.009</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>Temkin</td>
<td>KT (mmol dm⁻³)</td>
<td>15.24±8.23</td>
<td>10.39±2.81</td>
<td>25.28±10.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (kJ mol⁻¹)</td>
<td>4.19±0.69</td>
<td>4.59±0.42</td>
<td>5.85±0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R^2</td>
<td>0.840</td>
<td>0.943</td>
<td>0.916</td>
</tr>
<tr>
<td></td>
<td></td>
<td>χ^2</td>
<td>0.006</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>Langmuir</td>
<td>Nf (mmol g⁻¹)</td>
<td>0.83</td>
<td>0.63</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ns (mmol g⁻¹)</td>
<td>0.91±0.02</td>
<td>0.74±0.03</td>
<td>0.61±0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (g mmol⁻¹)</td>
<td>2.94±0.32</td>
<td>1.83±0.36</td>
<td>3.97±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R^2</td>
<td>0.979</td>
<td>0.890</td>
<td>0.906</td>
</tr>
<tr>
<td></td>
<td></td>
<td>χ^2</td>
<td>0.001</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>60</td>
<td>Freundlich</td>
<td>Kf (mmol g⁻¹)</td>
<td>0.60±0.03</td>
<td>0.45±0.02</td>
<td>0.46±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n</td>
<td>3.98±0.73</td>
<td>4.13±0.88</td>
<td>5.68±1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R^2</td>
<td>0.847</td>
<td>0.736</td>
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<tr>
<td></td>
<td></td>
<td>χ^2</td>
<td>0.009</td>
<td>0.006</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Temkin</td>
<td>KT (mmol dm⁻³)</td>
<td>45.09±19.62</td>
<td>28.34±18.20</td>
<td>189.65±23.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b (kJ mol⁻¹)</td>
<td>6.02±0.66</td>
<td>7.25±1.21</td>
<td>11.17±2.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R^2</td>
<td>0.921</td>
<td>0.801</td>
<td>0.798</td>
</tr>
<tr>
<td></td>
<td></td>
<td>χ^2</td>
<td>0.005</td>
<td>0.004</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Fig. 3.10  Linear form of Langmuir sorption isotherm for copper (■) lead (●) and Nickel (▲)
On activated carbon prepared at 673 K for (a) 30  (b) 45 and (c) 60 min.
Figure 3.11 Experimental and nonlinear (■) Langmuir (●), Freundlich (○) and Temkin (▼) sorption isotherm for copper on activated carbon prepared at 30 min.
3.5 Elemental analysis of chemically modified chitosan

Pristine chitosan (CH) and chemically modified chitosan with acryloylmorpholine (CHAM) were analyzed for carbon and nitrogen by elemental analysis. The calculated amount of the elements and their relationship are given in Table 3.8. The general amount of each element (L₀) attached in the pendant chains were calculated using expression 10. Acryloylmorpholine molecule contains six carbons and nitrogen resulting in increased amount of both the nitrogen and carbon content in the chemically modified chitosan. These values reflect the incorporation of acryloylmorpholine moiety as a pendant chain in the precursor chitosan backbone.

\[
L_0 = \frac{\text{% Element}}{\text{Atomic mass of element}} \times 10
\]  

(10)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C/%</th>
<th>N/%</th>
<th>C/mmolg⁻¹</th>
<th>N/mmolg⁻¹</th>
<th>C/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>40.63</td>
<td>7.39</td>
<td>33.86</td>
<td>5.27</td>
<td>6.42</td>
</tr>
<tr>
<td>CHAM</td>
<td>41.99</td>
<td>7.67</td>
<td>34.99</td>
<td>5.48</td>
<td>6.38</td>
</tr>
</tbody>
</table>
3.6 Infrared spectroscopy of chemically modified chitosan

The FTIR spectrum of the ancestor chitosan shows absorption bands at 1076, 1379 and 1419, 3400, 2916 and 2877, 1655 and 1597 cm\(^{-1}\) demonstrating the presence of C—O, C=O, OH and NH\(_2\), C—H, amide I and N-H groups, respectively [189]. While the spectrum for the altered polymer had given several spectral changes as compared to the originator as shown in Fig. 3.12. The bands for amide I and N-H, have given improved concentration and have turn into larger which confirms the anticipated chemical alteration.

![Infrared spectra of chitosan CH and chemically modified chitosan CHAM.](image)

**Fig. 3.12** Infrared spectra of chitosan CH and chemically modified chitosan CHAM.
3.7 Nuclear magnetic resonance spectra of chemically modified chitosan

The $^{13}$C NMR spectra for pure chitosan and the chemically tailored one are given away in Fig. 3.13. NMR signals were observed at 75 and 62, 84, 57, 105 and at 19 and 175 ppm indicating the presence $\text{C3/C5}, \text{C6}, \text{C4}, \text{C2}$ and $\text{C1}$ respectively for the precursor chitosan [190]. The tailored chitosan offered peaks at 57 and 62 ppm demonstrating the presence of $\text{C2}$ and $\text{C6}$. These peaks are finely alienated because of improved number of carbon and nitrogen bonds. Which additionally validates the anticipated chemical alteration.

\[\text{Fig. 3.13} \ 13\text{C NMR spectra in solid state of chitosan CH and chemically modified chitosan CHAM}\]
3.8 Thermogravimetry of chemically modified Chitosan

Thermal analysis of ancestor chitosan evidently show two dealings as demonstrated in Fig 3.14. The first phase of breakdown take place at 335 K with a loss of 9 % of its mass, while the second phase at 570 K with 57% of loss in its mass. The first step representing water removal and the second change at 570 K is for chitosan disintegration [191]. For chemically tailored chitosan the slightly lower value of the first and second decomposition stages were observed compare with precursor chitosan, indicating a moderate degree of fictionalization. The derivative profile for lly tailored chitosan showed the first peak at 331 K for water loss and showing 11% mass loss. At 565 K the second breakdown, for modified one, occurred with 50% a mass loss as shown in Fig. 3.15. The temperature of second decomposition stage for chemically modified chitosan is lower, however lower loss of mass occurs at this stage compare to precursor chitosan showing more thermal stability because of alteration, signifying dissimilarity between them.

![Thermogravimetric and derivative curves for chitosan CH](image)
3.9 Scanning electron microscopy of chemically modified Chitosan
The predecessor chitosan has even feathery exterior with a bit folding structure. While customized chitosan has exclusively diverse morphology and its exterior is allied in a non-uniform and unbalanced manner as revealed in Fig. 3.16a and 3.16b.
Fig. 3.16a. SEM image of chitosan CH

Fig. 3.16b. SEM image of chemically modified chitosan CHAM
3.10 Sorption studies of chemically modified chitosan

The sorption isotherms are fundamental in understanding the mechanism of sorption. Important informations such as how the sorbate molecules are distributed between the liquid/solid phases at the equilibrium state can be interpreted from sorption isotherms. The Langmuir, Freundlich and Temkin isothermal equations were used to describe the sorption equilibrium of lead, copper and cadmium ions onto chemically modified chitosan.

The sorption capacity of chemically modified chitosan was higher for copper than that of lead and cadmium as shown in Table 3.9. It is to be noted that the higher sorption capacity for copper is due to Hard/Soft acid base interactions [192]. Nitrogen is a border line Lewis basic center and copper is also a border line metal. As a result, chemically modified chitosan showed higher sorption capacity for copper (3.35 mmol g\(^{-1}\)) than lead (1.60 mmol g\(^{-1}\)) and cadmium (0.74 mmol g\(^{-1}\)) as shown in Fig. 3.17. The sorption capacities of chemically modified chitosan were also higher than precursor chitosan for copper 1.60 and lead 1.19 mmol g\(^{-1}\). However the sorption capacity of chitosan was higher for lead 1.35 mmol g\(^{-1}\) than chemically modified chitosan. The order of sorption was Cu > Pb > Cd. The linear form of Langmuir sorption isotherm for metals studied is shown in Fig. 3.18.
Table 3.9. Number of moles sorbed ($N_f$), parameters of the Langmuir ($N_s$ and $b$), coefficients determination ($R^2$) and standard errors (SE) for the interaction of divalent metals with modified chitosan CHAM, at 298 ± 1 K using linear method.

<table>
<thead>
<tr>
<th>Material</th>
<th>Metal ions</th>
<th>Parameter</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>3.35</td>
<td>3.35</td>
<td>3.35</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>3.55±0.01</td>
<td>3.21±0.01</td>
<td>3.38±0.09</td>
<td>3.43±0.61</td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$</td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.94±0.004</td>
<td>3.51±0.002</td>
<td>3.03±0.02</td>
<td>2.89±0.22</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.989</td>
<td>0.946</td>
<td>0.946</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>SE</td>
<td>0.22</td>
<td>0.36</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Pb$^{2+}$</td>
<td>$\chi^2$</td>
<td>0.210</td>
<td>0.13</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>1.60</td>
<td>1.60</td>
<td>1.60</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.81±0.11</td>
<td>1.62±0.05</td>
<td>1.79±0.08</td>
<td>1.84±0.04</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>0.42±0.01</td>
<td>0.52±0.05</td>
<td>0.43±0.21</td>
<td>0.40±0.03</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>$R^2$</td>
<td>0.996</td>
<td>0.984</td>
<td>0.934</td>
<td>0.934</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>SE</td>
<td>0.16</td>
<td>0.11</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Cd$^{2+}$</td>
<td>$\chi^2$</td>
<td>0.24</td>
<td>0.08</td>
<td>0.07</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Fig. 3.17. Experimental sorption isotherm of chemically modified chitosan CHAM for (a) lead (▼), cadmium (●) and (b) copper (■).
Different linear forms of the Langmuir models gave different values of constants and distribution of errors as shown in Table 3. In case of copper and lead the differences between constants are higher because of different linear forms of Langmuir model. Different axial arrangements also change distribution of error that alters the theory behind the isotherm. However, in case of cadmium the value of $N_s$ and $b$ are very close to each other, so it means that experimental factors also involved in different values of constants. The lowest standard error and chi-square test were found for the Langmuir model type IV for all the metals under studies. Error functions of the Freundlich model was higher than the Langmuir model showing that it does not fit better to experimental data, however in case of the Temkin model smallest value of standard error and chi-square test was found, it shows that this model fits better to experimental data than Langmuir and Freundlich model as shown in Table 3.10
Table 3.10. Number of moles sorbed \((N_f)\), the Freundlich \((n \text{ and } K_f)\), the Temkin \((b \text{ and } K_T)\), Langmuir \((N_s \text{ and } b)\) parameters, coefficient determination \((R^2)\) and respective error for interaction of divalent metals with CHAM at 298 ± 1 K, using linear method.

<table>
<thead>
<tr>
<th>Method</th>
<th>Isotherm</th>
<th>Parameters</th>
<th>Cu(^{2+})</th>
<th>Pb(^{2+})</th>
<th>Cd(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freundlich</td>
<td>(K_f \text{ (mmol g}^{-1}))</td>
<td>1.81±0.01</td>
<td>0.51±0.03</td>
<td>0.43±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(n)</td>
<td>2.69±0.02</td>
<td>2.18±0.04</td>
<td>3.80±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>0.952</td>
<td>0.939</td>
<td>0.959</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.51</td>
<td>0.95</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td>Linear</td>
<td>(\chi^2)</td>
<td>18.78</td>
<td>9.16</td>
<td>33.21</td>
</tr>
<tr>
<td></td>
<td>Temkin</td>
<td>(K_T \text{ (mmol dm}^{-3}))</td>
<td>28.38±0.06</td>
<td>4.74±0.04</td>
<td>93.39±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b \text{ (kJ mol}^{-1}))</td>
<td>1.596±0.04</td>
<td>0.923±0.04</td>
<td>0.272±0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>0.962</td>
<td>0.966</td>
<td>0.958</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE</td>
<td>0.217</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\chi^2)</td>
<td>0.26</td>
<td>0.08</td>
<td>0.008</td>
</tr>
</tbody>
</table>

However, the values of different error functions corresponding to the non-linear Langmuirequation are smaller than those of the Freundlich and the Temkin models as shown in Table 3.11.
Table 3.11. Number of moles sorbed ($N_f$), parameters of the Freundlich ($n$ and $K_f$), Temkin ($K_T$ and $b$), coefficients of determination ($R^2$) and respective error for interaction of Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ with chitosan, CHAM at 298 ± 1 K, using non-linear method.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameters</th>
<th>Cu$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Cd$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$N_f$ (mmol g$^{-1}$)</td>
<td>3.35</td>
<td>1.60</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>$N_s$ (mmol g$^{-1}$)</td>
<td>1.87±0.05</td>
<td>1.87±0.05</td>
<td>0.77±0.006</td>
</tr>
<tr>
<td></td>
<td>$b$ (g mmol$^{-1}$)</td>
<td>1.61±0.2</td>
<td>0.38±0.03</td>
<td>1.69±0.08</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.984</td>
<td>0.990</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.02</td>
<td>0.003</td>
<td>0.0001</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$ (mmol g$^{-1}$)</td>
<td>3.64±0.1</td>
<td>1.87±0.05</td>
<td>0.77±0.006</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>3.35±0.45</td>
<td>2.83±0.40</td>
<td>5.82±0.65</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.920</td>
<td>0.918</td>
<td>0.917</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.11</td>
<td>0.02</td>
<td>0.001</td>
</tr>
<tr>
<td>Temkin</td>
<td>$K_T$ (mmol dm$^{-3}$)</td>
<td>28.50±7.28</td>
<td>4.74±0.98</td>
<td>93.16±43.50</td>
</tr>
<tr>
<td></td>
<td>$b$ (kJ mol$^{-1}$)</td>
<td>1.55±0.10</td>
<td>0.965±0.17</td>
<td>0.295±0.73</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.966</td>
<td>0.970</td>
<td>0.950</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.04</td>
<td>0.009</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Non-linear regression analysis corresponds in the best way to select the isotherm that fits the experimental data. This method involves an attempt to minimize the distribution of errors between experimental data and the isotherm considered as shown in Fig. 3.19. Both linear and non-linear regression analysis produce different models as the best fitting isotherm for the given set of data, thus indicating a significant difference between the analytical methods.
3.11 Kinetic Study

Kinetics study enlightens the rate of uptake of cations on chemically modified chitosan and the time required to reach equilibrium. It can be observed that sorption of copper and cadmium achieve equilibrium within 3 h and maximum sorption capacity for copper reached to 3.35 mmol g\(^{-1}\) as shown in Fig. 3.20.
In case of lead the sorption system achieve equilibrium within 4 h. The 1st order (pseudo) order [193] and 2nd order (pseudo) [194] were applied to predict the sorption kinetic process as shown in equation 9 and 10.

$$\log(N_f - N_{ft}) = \log N_f - (\frac{k_1}{2.303})t$$  \hspace{1cm} (11)

Where $k_1$ is the rate constant for 1st order (min$^{-1}$) of sorption, $N_f$ and $N_{ft}$ (mmol/g) are the amount of metal ion sorbed at equilibrium and time $t$ (min), respectively. The $N_f$ and $k_1$ is calculated by plotting the log ($N_f/N_{ft}$) versus $t$ shows second order sorption. The plot of log ($N_f/N_{ft}$) versus $t$ for cadmium sorption on chemically modified chitosan is shown in Fig. 3.21.
The pseudo-second-order model can be written as follow:

$$\frac{t}{Nft} = \frac{1}{K \cdot Nf^2} + \left(\frac{1}{Nf}\right)t$$

(12)

Where $k_2 \text{ (g/mg min)}$ is the rate constant for second order. Second order's parameters are calculated from the plots of $(t/Nft)$ versus $t$. The calculated $Nf$ values agree very well with experimental values and high value of regression coefficient confirms that the sorption phenomena followed second order kinetics. The $1^{st}$ order caters a decent results, relatively smaller error value; however, higher correlation coefficient (Table 3.12) of the $2^{nd}$ order (pseudo) suggested that this could better depict the sorption of copper, lead and cadmium. The value of $Nf$ calculated from pseudo second order equation is very close to experimental sorption of cations on chemically modified chitosan. These values indicate a better fit of pseudo-second-order model with the experimental data as compared to the first-order model.
Table 3.12 Rate constants for two kinetic models for chemically modified chitosan (CHAM).

<table>
<thead>
<tr>
<th>Metal</th>
<th>$N_f$ (mmol g$^{-1}$)</th>
<th>$K_1$ (10$^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>$N_f$ (mmol g$^{-1}$)</th>
<th>$K_2$ (10$^{-3}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>7.14</td>
<td>2.58</td>
<td>0.890</td>
<td>4.63</td>
<td>2.34</td>
<td>0.967</td>
</tr>
<tr>
<td>Pb</td>
<td>1.88</td>
<td>1.46</td>
<td>0.956</td>
<td>2.46</td>
<td>3.29</td>
<td>0.966</td>
</tr>
<tr>
<td>Cd</td>
<td>0.63</td>
<td>2.93</td>
<td>0.938</td>
<td>0.79</td>
<td>78.9</td>
<td>0.998</td>
</tr>
</tbody>
</table>
CONCLUSIONS

*Salvadora persica* was converted into powdered form and characterized by using Infrared spectroscopy. It has various organic compounds and these compounds contain sulphur, oxygen and nitrogen in their skeletons and behaved superbly as coordinating ligands for cations present in the aqueous solution and hence caused effective sorption. The Freundlich, Langmuir and Temkin models (both linear and non-linear methods) were used to assess the experimental statistics. Among these cations copper showed highest sorption ability as compared to other and the sorption properties were in agreement with that of the Langmuir (I).

Activated carbon was also prepared from *Salvadora persica* under vacuum at 400 °C with different soaking time. The prepared activated carbons were characterized using Surface Area Analyzer. Percentage yield of the prepared activated carbons in different heating times prior to washing was different. The activated carbon yields obtained at 400 °C were 54.78 %, 52.27 % and 50.31 % at 30, 45 and 60 min heating time respectively. The yield of activated carbons decreased as the heating duration increased, surface area also decreased. The activated carbon prepared at 30 min heating time, showed maximum sorption capacities for cations due to its larger surface area. The Freundlich, Langmuir and Temkin models (both linear and non-linear methods) were used to assess the experimental statistics. For activated carbon, lower errors were shown by type one (I) of the Langmuir I as compared to Freundlich and Temkin models, so it is the appropriate model to explain the sorption phenomenon.

4-acryloylmorpholine was reacted with chitosan to alter it chemically. The aim of treatment was to add in binding sites for heavy metal ions. The amended chitosan holds different binding sites (chelating centers) in the form of oxygen and nitrogen. Different techniques were applied to illustrate the amended chitosan. Chitosan and the chemically modified chitosan were used as sorbents for different cations (Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$). Among these cations copper showed highest sorption ability as compared to other. Among the linear forms of the Langmuir isotherms, low error values were given by type four (IV) than other linear forms of the Langmuir and than the Freundlich model but higher than that of Temkin model, which shows that Temkin model fits better to the experimental data of chemically modified chitosan.
REFERENCES


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Appendix A: Experimental and Linear

Linear Langmuir I for Cu on activated carbon 30

Linear Langmuir II for Cu on activated carbon 30
Linear Langmuir III for Cu on activated carbon 30

Linear Langmuir IV for Cu on activated carbon 30
Experimental for Cu on activated carbon 30

Linear Temkin for Cu on activated carbon 30
Linear Freundlich for Cu on activated carbon 30

Linear Langmuir I for Pb on activated carbon 30
Linear Langmuir II for Pb on activated carbon 30

Linear Langmuir III for Pb on activated carbon 30
Linear Langmuir IV for Pb on activated carbon 30

Experimental for Pb on activated carbon 30
Linear Temkin for Pb on activated carbon 30

Linear Freundlich for Pb on activated carbon 30
Linear Experimental for Ni on activated carbon 30

Linear Langmuir I for Ni on activated carbon 30
Linear Langmuir II for Ni on activated carbon 30

Linear Langmuir III for Ni on activated carbon 30
Linear Langmuir IV for Ni on activated carbon 30

Linear Temkin for Ni on activated carbon 30
Linear Freundlich for Ni on activated carbon 30

Linear Experimental for Cu on activated carbon 45
Linear Langmuir I for Cu on activated carbon 45

Linear Langmuir II for Cu on activated carbon 45
Linear Langmuir III for Cu on activated carbon 45

Linear Langmuir IV for Cu on activated carbon 45
Linear Freundlich for Cu on activated carbon 45

Linear Temkin for Cu on activated carbon 45
Experimental for Pb on activated carbon 45

Linear Langmuir I for Pb on activated carbon 45
Linear Langmuir II for Pb on activated carbon 45

Linear Langmuir III for Pb on activated carbon 45
Linear Langmuir IV for Pb on activated carbon 45

Linear Temkin for Pb on activated carbon 45
Linear Freundlich for Pb on activated carbon

Experimental for Ni on activated carbon
Linear Langmuir II for Ni on activated carbon 45

Linear Langmuir III for Ni on activated carbon 45
Linear Langmuir IV for Ni on activated carbon 45

Linear Temkin for Ni on activated carbon 45
Linear Freundlich for Ni on activated carbon

Experimental for Cu on activated carbon
Linear Langmuir I for Cu on activated carbon 60

Linear Langmuir II for Cu on activated carbon 60
Linear Langmuir III for Cu on activated carbon 60

Linear Langmuir IV for Cu on activated carbon 60
Linea Temkin for Cu on activated carbon 60

Linear Freundlich for Cu on activated carbon 60
Experimental for Pb on activated carbon 60

Linear Langmuir I for Pb on activated carbon 60
Linear Langmuir II for Pb on activated carbon 60

Linear Langmuir III for Pb on activated carbon 60
Linear Langmuir IV for Pb on activated carbon 60

Lizznear Temkin for Pb on activated carbon 60
Linear Freundlich for Pb on activated carbon 60

Experimental for Ni on activated carbon 60
Linear Langmuir I for Ni on activated carbon 60

Linear Langmuir II for Ni on activated carbon 60
Linear Langmuir III for Ni on activated carbon 60

Linear Langmuir IV for Ni on activated carbon 60
Linear Temkin for Ni on activated carbon

Linear Freundlich for Ni on activated carbon
Experimental for Cu on salvadora

Linear Langmuir I for Cu on salvadora
Linear Langmuir II for Cu on salvadora

Linear Langmuir III for Cu on salvadora
Linear Langmuir IV for Cu on salvadora

Linear Temkin for Cu on salvadora
Linear Freundlich for Cu on salvadora

Experimental for Pb on salvadora
Linear Langmuir I for Pb on salvadora

Linear Langmuir II for Pb on salvadora
Linear Langmuir III for Pb on salvadora

Linear Langmuir IV for Pb on salvadora
Linear Temkin for Pb on salvadora

Linear Freundlich for Pb on salvadora
Experimental for Ni on salvadora

Linear Langmuir I for Ni on salvadora
Linear Langmuir II for Ni on salvadora

Linear Langmuir III for Ni on salvadora
Linear Langmuir IV for Ni on salvadora

Linear Temkin for Ni on salvadora
Linear Freundlich for Ni on salvadora

Experimental for Cd on CHAM
Linear Langmuir I for Cd on CHAM

Linear Langmuir II for Cd on CHAM
Linear Langmuir III for Cd on CHAM

Linear Langmuir IV for Cd on CHAM
Linear Temkin for Cd on CHAM

Linear Freundlich for Cd on CHAM
Experimental for Cu on CHAM

Linear Langmuir I for Cu on CHAM
Linear Langmuir II for Cu on CHAM

Linear Langmuir III for Cu on CHAM
Linear Langmuir IV for Cu on CHAM

Linear Temkin for Cu on CHAM
Linear Freundlich for Cu on CHAM

Experimental for Pb on CHAM
Linear Langmuir I for Pb on CHAM

Linear Langmuir II for Pb on CHAM
Linear Langmuir III for Pb on CHAM

Linear Langmuir IV for Pb on CHAM
Linear Temkin for Pb on CHAM

Linear Freund for Pb on CHAM
APENDIX B: NON LINEAR LANGMUIR, TEMKIN AND FREUNDLICH

Non-Linear.Freundlich for Cu on activated carbon 30

Non-Linear.Temkin for Cu on activated carbon 30
Non-Linear Langmuir for Cu on activated carbon 30

Non-Linear Langmuir for Pb on activated carbon 30
Non-Linear Freundlich for Pb on activated carbon 30

Non-Linear Temkin for Pb on activated carbon 30
Non-Linear Langmuir for Ni on activated carbon 30

Non-Linear Temkin for Ni on activated carbon 30
Non-Linear Freundlich for Ni on activated carbon 30

Non-Linear Langmuir for Cu on activated carbon 45
Non-Linear Temkin for Cu on activated carbon

Non-Linear Freundlich for Cu on activated carbon
Non-Linear Langmuir for Pb on activated carbon

Non-Linear Temkin for Pb on activated carbon
Non-Linear Freundlich for Pb on activated carbon

Non-Linear Langmuir for Ni on activated carbon
Non-Linear Temkin for Ni on activated carbon 45

Non-Linear Freundlich for Ni on activated carbon 45
Non-Linear Temkin for Cu on activated carbon 60

Non-Linear Freundlich for Cu on activated carbon 60
Non-Linear Langmuir for Cu on activated carbon 60

Non-Linear Langmuir for Pb on activated carbon 60
Non-Linear Temkin for Pb on activated carbon 60

Non-Linear Freundlich for Pb on activated carbon 60
Non-Linear Langmuir for Ni on activated carbon 60

Non-Linear Temkin for Ni on activated carbon 60
Non-Linear Freundlich for Ni on activated carbon 60

Non-Linear Langmuir for Cu on salvadora
Non-Linear Temkin for Cu on salvadora

Non-Linear Freundlich for Cu on salvadora
Non-Linear Temkin for Pb on salvadora

Non-Linear Langmuir for Pb on salvadora
Non-Linear Freundlich for Pb on salvadora

Non-Linear Langmuir for Ni on salvadora
Non-Linear Temkin for Ni on salvadora

Non-Linear Freundlich for Ni on salvadora
Non-Linear Langmuir for Cd on CHAM

Non-Linear Temkin for Cd on CHAM
Non-Linear Freundlich for Cd on CHAM

Non-Linear Langmuir for Cu on CHAM
Non-Linear Temkin for Cu on CHAM

Non-Linear Freundlich for Cu on CHAM
Non-Linear Langmuir for Pb on CHAM

Non-Linear Temkin for Pb on CHAM
Non-Linear Freundlich for Pb on CHAM
APENDIX C: FOR CALCULATED LANGMUIR, TEMKIN AND FREUNLICH

Exp. ■, Lang I●, II ○,III * and IV▲ for Cu on activated carbon 30

Exp■, Temkin▲ and Freund ● for Cu on activated carbon 30
Exp ■, Lang I ●, II ○, III * and IV ▲ for Pb on activated carbon 30

Exp ■, Temkin ▲ and Freund ● for Pb on activated carbon 30
Exp ■, Lang I ●, II ○, III * and IV ▲ for Ni on activated carbon 30

Exp ■, Temkin ▲ and Freund ● for Ni on activated carbon 30
Exp. Lang I ●, II ○, III * and IV ▲ for Cu on activated carbon 45

Exp. Temkin ▲ and Freund ● for Cu on activated carbon 45
Exp. ■, Lang I ●, II ○, III * and IV ▲ for Pb on activated carbon

Exp. ■, Temkin ▲ and Freund ● for Pb on activated carbon
Exp■, Lang I ●, II ○, III* and IV▲ for Ni on activated carbon 45

Exp ■, Temkin ▲ and Freund. ● for Ni on activated carbon 45
Exp ■, Lang I ●, II ○, III* and IV ▲ for Cu on activated carbon 60

Exp ■, Temkin ▲ and Freund ● for Cu on activated carbon 60
Exp ■, Lang I ●, II ○, III and ▲ IV for Pb on activated carbon 60

Exp ■, Temkin ▲ and Freund ● for Pb on activated carbon 60
Exp ■. Lang I●, II ○, III ○ and IV ▲ for Ni on activated carbon 60

Exp ■. Temkin ▲ and Freund ● for Ni on activated carbon 60
Exp ■, Lang I ●, II ○, III* and IV ▲ for Cu on salvadora

Exp ■, Temkin ▲ and Freund ● for Cu on salvadora
Exp■, .Lang I ●,II ○,III * and IV ▲ for Pb on salvadora

Exp ■.Temkin ▲ and Freund ● for Pb on salvadora
Exp ■.Lang I●,II○,III* and IV▲ for Ni on salvadora

Exp ■.Temkin▲ and Freund● for Ni on salvadora
Exp. Lang I●, II○, III* and IV▲ for Cd on CHAM

Exp. Temkin ▲ and Freund ● for Cd on CHAM
Exp ■. Lang I ●, II ○, III * and IV ▲ for Cu on CHAM

Exp ▲. Temkin ▲ and Freund ● for Cu on CHAM
Exp ■, Lang I●,II○,III * and IV▲ for Pb on CHAM

Exp ■, Temkin▲ and Freund● for Pb on CHAM