

**ADSORPTIVE SEPARATION OF HEAVY METALS ONTO XANTHATED  
APPLE WASTE FROM AQUEOUS SOLUTION**

**A Dissertation**

**Submitted in partial fulfillment of requirements for the Degree of Master of  
Science in Chemistry**

*by*  
**Deepak Bashyal**

**Central Department of chemistry  
Institute of Science and technology  
Tribhuvan University  
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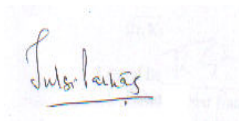
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Institute of Science and Technology  
Central Department of Chemistry  
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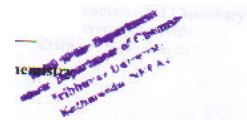
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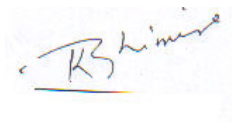
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Central Department of Chemistry**



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**External examiner**



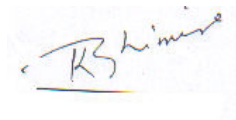
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**Supervisor  
Dr. Kedar Nath Ghimire  
Lecturer  
Central Department of Chemistry**

## Foreword

The dissertation entitled "*Adsorption of heavy metals onto xanthated apple waste from aqueous solution*" submitted by Mr. Deepak Bashyal for the M. Sc. degree in Chemistry of Tribhuvan University is carried out under my supervision.

During the research period he has worked sincerely and satisfactorily to complete this dissertation. He had presented this paper in "Chemical congress 2008". No part of this thesis has been submitted for any other degree.



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**Dr. Kedar Nath Ghimire**  
**Lecturer**  
**Central Department of Chemistry**  
**Tribhuvan University**  
**Kritipur, Kathmandu**  
**Nepal**

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## Abstract

Biosorption is potentially an attractive technology for the treatment of wastewater retaining heavy metals in aqueous solution. This study investigated the feasibility of chemically modified apple waste as a novel type of biosorbent for lead, cadmium, zinc and Iron removal from aqueous medium. Xanthated apple waste as a biosorbent was prepared by simple chemical reaction with carbon disulphide under alkaline condition. The maximum exchangeable cations of the H<sup>+</sup>-form xanthated apple waste (XAW-gel) were as high as 2.52 mol/kg. The effect of pH, sorption kinetics, effect of competitive ion and isotherm were studied by batch method. The significant effect of pH was in the range of 3 to 6. Time dependency experiments for the metal ions uptake showed the biosorption rate was fast initially for 2h, followed by slow attainment of equilibrium. Sorption isotherm test showed that equilibrium sorption data were better represented by Langmuir model than the Freundlich model, and the maximum adsorption capacity of Pb(II), Cd(II), Zn(II) and Fe(III) were found to be 250, 192.30, 123.45 and 62.89 mg/g respectively. The pseudo first-order, pseudo second-order, and second-order models were used to analyze the kinetic data. The good correlation coefficient was obtained for pseudo second-order kinetic model. XAW-gel was found to be more efficient than the conventionally used adsorbent activated carbon and other most of the biosorbent. Based on the result, a judicious choice of modification strategy for raw apple waste precursors can produce adsorbent with active xanthated surface functional groups and appears to be a promising biosorbent for removal of heavy metals from aqueous water.

## Abbreviations

|         |  |
|---------|--|
| Fe(III) | Ferric iron  |
| Cd(II)  | Divalent cadmium                                   |
| Zn(II)  | Divalent zinc                                      |
| Pb(II)  | Divalent lead                                      |
| h       | Hour   |
| mg/l    | Milligram per liter                                |
| g/L     | Gram per liter                                     |
| mg/g    | Milligram per gram                                 |
| A%      | Adsorption efficiency                              |
| V       | Volume in milliliter                               |
| W       | Mass of the adsorbent in gram                      |
| ml      | Milliliter   |
| $C_i$   | Initial concentration of metal in mg/L             |
| $C_t$   | Concentration at time 't' in mg/L                  |
| $q_t$   | Amount of metal ion adsorbed at time 't' in mg/g   |
| $q_e$   | Amount of metal ion adsorbed at equilibrium time   |
| D       | Distribution ratio                                 |
| $q_m$   | Amount of metal to form monolayer coverage in mg/g |
| b       | Energy of adsorption in L/mg                       |
| K       | Adsorption capacity in L/g                         |
| n       | Adsorption intensity                               |
| mmol    | Milimole   |
| $k_1$   | pseudo first-order rate constant in L/mg           |
| $k_2$   | pseudo second-order rate constant in g/mg min      |
| $k_2'$  | Second-order rate constant in g/mg min             |
| $v_0$   | Initial adsorption rate in mg/g min                |
| XAW     | Xanthated Apple waste                              |
| $R^2$   | Coefficient of determination                       |
| A.C     | Activated carbon                                   |
| R. H    | Rice husk  |

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## **1.0 Introduction**

### **1.1 General introduction**

Water pollution due to excessive release of heavy metals in the environment has been a major cause of concern worldwide today. Heavy metal pollution occurs in industrial wastewater, such as those produced by metal plating facilities, battery manufacturing process, in the production of paints and pigments and glass industries [1], as well as in natural ground water. This wastewater commonly includes copper(Cu), nickel(Ni), chromium(Cr), cobalt(Co), arsenic(As), mercury(Hg). In addition cadmium(Cd), lead(Pb), zinc(Zn) and iron(III) are commonly detected in both natural and industrial effluents. These heavy metals are not biodegradable and their presence in stream and lakes leads to bioaccumulation in living organism [18], causing health problems in animals, plants and human beings.

#### **Hazardous effect of lead, cadmium, zinc and iron**

Cadmium and lead are the two important member of the “big three” toxic heavy metals (Pb, Hg, Cd) mainly originating from electroplating, battery manufacturing and other industrial operations. The drinking water guidelines value recommended by World Health Organization (WHO) for Pb and Cd is 0.010 mg/L and 0.005 mg/L respectively.

Cadmium mainly accumulates in liver and kidney, which will malfunction at overdoses, spilling proteins in the urine and disrupting protein metabolism. While bones heart testes and hamatopoietic system were affected and these organs functions are impaired and anemia is frequently observed at chronic exposure. On the other hand the presence of ubiquitous lead causes serious toxicological concern. Lead when once absorbed, it passes into the blood streams where more than 95% is bound to the erythrocytes causing increased ‘fragility’ and reduced life span of the cells. Acute and classical lead poisoning in human adults is manifested by anemia, wrist, foot drop, renal and sperm damage.

Similarly zinc and iron are presence in ground as well as industrial waste water. Zinc and iron, are the essential trace elements in plants and animal life for



metabolism and are common elements presents in mine rocks and soil and hence most natural water contains some iron and zinc in dissolved form. Nevertheless both of these element and their compounds are not entirely free of hazard; and at overdoses can cause severe effect. The guidelines value of iron and zinc as recommended by WHO in natural drinking water is 0.2-0.3 mg/L and 1.50 mg/L respectively. In real sense the requirement depends upon age of the person. Generally 10 – 50 mg/day is unlikely to cause adverse effect. The problems created by high iron concentration are mainly aesthetic.

Zinc is relatively nontoxic; hazardous is mainly due to anion or associated metal like acidic solution of  $ZnCl_2$  and  $ZnSO_4$ . Very High concentration of zinc such as 500 mg/L or more can cause diarrhea, vomiting, nausea, hypocalcaemia, bone resorption, permanent damages and abdominal disorder.

To remove these toxic heavy metals from aqueous solution conventional method such as chemical precipitation, electrolytic recovery, ion exchange/chelation, evaporation and solvent extraction/liquid membrane separation are in practice. Application of these methods however is not widely practiced, because of economical and technical viability as these methods causes a significant disposal problem [1, 18] and is suitable only for high concentration treatment.

The method commonly used to remove toxic heavy metals from aqueous medium are based on the adsorption of ions onto insoluble compound and the separation of sediments formed. The activated carbon which is commonly used as adsorbent for the removal of various heavy metals from aqueous solution. In spite of its effectiveness in the removal of heavy metals from aqueous medium at low concentration, the high cost of activated carbon has restricted its more widespread use. Hence an economical and easily available adsorbent would certainly make an adsorption-based process a viable alternative for the treatment of water containing heavy metals [15].

In a view of such regard, recently biological method of heavy metal removal gained considerable momentum due to their high efficiency, low operating cost and simplicity [4]. One of such method is biosorption, in which

inactive biological material are utilized to sequester toxic heavy metals from aqueous solution [2]. The biological material that have been investigated for heavy metals include the agricultural and natural wastes as rice husk [18], coconut shell, saw dust, sugar beet [8], orange juice residue [15], sugarcane baggage, maize cob [12] etc, which are often considered as solid waste of agriculture and easily and widely available.

Biosorption of heavy metals by these biological materials involves several mechanisms that differ qualitatively and quantitatively depending on the species used, the origin of biomass and its processing procedure. There is also no need for complicated regeneration processes when using these agricultural byproduct and such materials are capable of binding with heavy metals by adsorption, chelation and ion exchange.

From such economical view point, the bio-waste material investigated in this study is an apple waste generated in juice centre. Apple waste contains cellulose, hemicelluloses, lignin, and lots of pectin in the cell wall as an intercellular cementing material [24]. Pectin is a polysaccharide, in which pectic acid, an acidic polysaccharide, is mainly composed of D-galacturonic acid and methyl ester [4, 13] is expected to utilize along with cellulose. However, since the content of active functional groups in the natural apple waste is considered not to be sufficient to strongly bind enough metal ion, the cellulose content of apple waste is subjected to xanthation in order to convert its abundant alcoholic hydroxyl groups into xanthate groups to enhance adsorption capacity for metal cations in aqueous solution. In fact for the application of this material; lead, cadmium zinc and iron are the focus in the study.

The oxygen atom in the active functional group of the pectin and cellulose can be classified as a hard ligand group having less affinity for heavy metals according to HSAB (Hard and soft acid and base) classification system [19]. If soft ligand group such as sulphur can be introduced onto this natural polysaccharide backbone, it will increase the uptake capacity for many heavy metals, because Pb(II), Cd (II), Zn(II) can be classified as soft acid, which have a strong affinity to soft ligand. Thus for potential application of such biomaterial,

chemical modification to introduce a variety of functional group is the latent key action. For this reason carbon-disulphide is used as a reagent to introduce xanthate group onto the starting material. Since sulphur has a very strong affinity for most heavy metals to create new chelating group to polymer backbone, alternatively ion-exchange may takes place between incoming cation and either sorbed metal ions or  $H^+$ -ions of the functional group at the sorbent surface. Materials with surface functional groups, such as xanthate group, shows improved selectivity for the removal of heavy metals in aqueous solution [3]. For this purpose we have developed an effective, simple and low cost alternative employing chelating agent with xanthate groups incorporated on apple waste.

The use of agricultural and natural wastes as biosorbent thus not only would provide a less costly sorbent to activated carbon or synthetic ion-exchangers, but also offers a potential alternative to conventional method for heavy metals removal [20]. On account of such possibility, the present study is based on the preparation and evaluation of efficiency of xanthated material from apple waste for the binding of divalent and trivalent metal ions: Pb(II), Cd(II), Zn(II) and Fe(III).

Apple is a most abundant fruit available at any season in the market. The residue generated as a waste during juicing at the juice centers is easily available as feed material.

## **1.2 Adsorption study**

Adsorption study is generally conducted to determine the adsorption behaviors for metals ion onto the adsorbent. The adsorption tests can be studied by batch wise and by using a column [4].

In the test using a column, metal removal is carried out in a glass column of particular length and internal diameter, packed with definite amount of sorbent. The column is conditioned by allowing effluent to flow through a reservoir at the top using flow controller [4]. The treated effluent samples are collected at definite interval of time to measure the corresponding residual metal ion concentration to evaluate the efficiency of column.

In the batch wise test, a definite mass of the dried adsorbent is equilibrated with solution containing different amount of heavy metals. The suspension is filtered and analyzed with the help of analyzer to determine the efficiency of adsorbent. The sorption capacity, extent of adsorption and the mechanism of adsorption is determined by changing any one of the parameter keeping other constant [15].

The adsorption efficiency A% of metal ion can be calculated by using formula [16],

$$A\% = \frac{(C_i - C_t)100}{C_i} \dots\dots\dots I$$

Where,  $C_i$  and  $C_t$  are the concentration of metal ion in (mg/L) at initially and at time 't' respectively.

The sorption capacity of metal ion is the concentration of metal ions on the adsorbent and can be calculated based on the mass balance principle as,

$$q_t = \frac{(C_i - C_t)V}{W \times 1000} \dots\dots\dots II$$

In this equation,  $q_t$  represents the amount of metal up taken per unit mass of adsorbent (mg/g) at time 't',  $V$  is the volume of test solution (ml),  $W$  is the mass of dry adsorbent (g),  $C_i$  and  $C_t$  are the concentration of metal solution in mg/L at initially and time 't' respectively.

At equilibrium,  $C_t = C_e$ ,  $q_t = q_e$ .

The distribution ratio (D), is defined as the ratio of the amount of adsorption to the metal ion concentration in aqueous solution at equilibrium, and is calculated according to equation III;

$$D = q_e/C_e \dots\dots\dots III$$

Where  $q_e$  is the equilibrium amount of adsorption of metal ion per unit mass of the adsorbent,  $C_e$  is the equilibrium concentration in (mg/L).

### 1.3 Adsorption isotherm

Adsorption isotherm is a curve which relates the amount of adsorbate adsorbed per unit mass of adsorbent to the amount of unadsorbed sorbet remaining in solution at equilibrium time. Several models have been developed to describe adsorption behaviors. Virtually the adsorption behaviour of heavy metal ions can be analyzed with the help of well-known models given by Langmuir and Freundlich.

The *Langmuir isotherm* model is most commonly used adsorption isotherm for the adsorption of a solute from a liquid, which involves homogenous surface sorption with the formation of monolayer on the adsorbent surface. The isotherm equation given by Langmuir (1916) can be expressed as [8],

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots\dots\dots IV$$

where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of the adsorbent (mg/g),  $q_m$  is the maximum uptake capacity of the sorbent or the number of moles of solute adsorbed per unit mass of the adsorbent in forming a complete monolayer on the surface be constant and temperature independent (mg/g), it is determined solely by the nature of the adsorbent,  $b$  is adsorption constant (L/mg) related to the energy of adsorption or net enthalpy. The value of  $b$  increases with strength of adsorption and decreases with temperature.  $C_e$  is the concentration of adsorbate in solution at equilibrium (mg/L).

To facilitate the fitting of model to experimental data and its parameter evaluation, the rearranged and linear form of Langmuir isotherm equation is given as,

$$\frac{C_e}{q_e} = 1/bq_m + C_e/q_m \dots\dots\dots V$$

From the experimental  $C_e$  and  $q_e$  data, the linear plot of  $C_e/q_e$  against  $C_e$  can be drawn to evaluate the Langmuir constant:  $q_m$  and  $b$ , from the slope and intercept for all metals. The values obtained from the Langmuir model ( $q_m$  and  $b$ ) can provide information in the screening of the sorbent. A high value of  $b$  indicates a

steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate.

The *Freundlich isotherm* model gives a adequate description of adsorption data over a restricted range of concentration, even though it a fairly empirical isotherm and not based on any theoretical background. The isotherm equation given by Freundlich (1906) can be expressed as,

$$q_e = KC_e^{1/n} \dots\dots\dots\text{VI}$$

The linear form of Freundlich isotherm equation is obtained by rearranging in logarithmic form as,

$$\log q_e = \log K + 1/n \log C_e \dots\dots\dots\text{VII}$$

Where,  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate(mg/L),  $K$  and  $n$  are Freundlich equilibrium coefficient related to adsorption capacity and adsorption intensity respectively, used to calculate the theoretical adsorption capacity of adsorbent for metals. This can be obtained from intercept and slope of the linear plot of  $\log C_e$  against  $\log q_e$  and the value of  $1/n < 1$  indicates the favorable adsorption.

Apart from a homogenous surface sorption, the Freundlich equation is also suitable for a highly non-ideal sorption that involves heterogeneous surface sorption and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption.

#### **1.4 Adsorption kinetics**

The adsorption kinetic is employed for the evaluation of biosorption kinetic rates. In order to define adsorption kinetics of heavy metal ions, the kinetic parameter for the adsorption process is studied by monitoring the percentage removal of the heavy metals by the adsorbent.

The kinetics of heavy metal adsorption can be modeled by the pseudo first-order, pseudo second-order and the second-order rate equation. The relationship

between experimental data and the model predicted value of Pb(II), Cd(II), Zn(II) and Fe(III) biosorption on apple waste is expressed by coefficient of determination ( $R^2$ ). This measures the degree of relationship between two sets of data and helps in evaluating, which reaction model is suitable for the adsorption of heavy metals onto adsorbent. A relatively high value of  $R^2$  (~1) indicates [20] the model successfully describes the kinetics of Pb(II), Cd(II), Zn(II) and Fe(III) adsorption.

**The pseudo first-order model**

The pseudo first order kinetic process is used for the reversible reaction with an equilibrium being established between liquid and solid phase. The pseudo first-order rate equation (Lagergren, 1898) to study the kinetics of heavy metal adsorption is given by,

$$dq_t/dt = k_1(q_e - q_t) \dots \dots \dots \text{VIII}$$

Where,  $q_e$  is the amount of metal ion adsorbed at equilibrium (mg/g) and  $q_t$  is the amount of metal ion adsorbed at any time 't' (mg/g).  $k_1$  is the Lagergren rate constant for adsorption ( $\text{min}^{-1}$ ).

The linearized form of the equation VIII; can be expressed after integrating and applying boundary conditions  $t = 0$  to  $t = t$ , and  $q_t = 0$  to  $q_t = q_t$ ,

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \dots \dots \dots \text{IX}$$

From the straight line plot of  $\log (q_e - q_t)$  against time 't' of equation IX; value of  $k_1$  and  $q_e$  can be determined with the help of slope and intercept, respectively.

**The pseudo second-order model**

The pseudo second-order rate equation can be tested for experimental data. It is based on the sorption capacity on the solid phase. The pseudo second-order reaction rate equation (Y. S. Ho and G. McKay, 1997) used to study the kinetics of adsorption of heavy metal is expressed as rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites;

$$dq/dt = k_2(q_e - q_t)^2 \dots \dots \dots \text{X}$$

Where,  $k_2$  is the rate constant for pseudo second-order adsorption (g/mg min),  $q_t$  and  $q_e$  are the amount of metals adsorbed (mg/g) at any time  $t$  and at equilibrium time respectively.

Integrating the equation x; under boundary condition,  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , gives rearranged linear form as,

$$t/q_t = 1/k_2q_e^2 + 1/q_e t \dots\dots\dots XI$$

If the initial adsorption rate is  $v_0$  (mg/g min) on account,

Then  $v_0 = k_2 q_e^2$

The equation xi; can be written as,

$$t/q_t = 1/v_0 + 1/q_e t \dots\dots\dots XII$$

From the linear plot of  $t/q_t$  against  $t$ ,  $q_e$  and  $k_2$  can be determined experimentally with the help of slope and intercepts of plot respectively

**The second-order model**

The second –order reaction rate equation (Lagergren, 1898) is generally expressed as,

$$dq/dt = k'_2(q_e - q_t)^2 \dots\dots\dots XIII$$

Where  $k'_2$  is the second-order rate constant for adsorption (g/mg min).

Integrating the equation xiii; under boundary condition, as  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$ , the linear form of equation xiii; becomes,

$$1/q_e - q_t = 1/q_e - k'_2 t \dots\dots\dots XIV$$

The plot of  $1/q_e - q_t$  against  $t$  gives linear plot, from which  $k'_2$  and  $q_e$  can be evaluated from the slope and intercepts respectively.

The validity of the kinetic models can be checked by studying the kinetics at different time interval with different initial metal concentration. The equilibrium uptake of metal should nearly equal to the experimental equilibrium. If it couldn't do so, then the reaction is not likely to be following that model, even if that particular model gives high correlation coefficient with the experimental data (Ho and McKay 1998).



Contrary to other well established model, pseudo second-order predicts the behaviour over the whole range of studies and it is in agreement with a chemisorption mechanism being the rate controlling step with the formation of monolayer coverage on the adsorbent surface (McKay *et al.*, 1999) [27].

## 1.5 Literature review

The presence and persistence of certain heavy metals in the water due to natural and industrial pollution is one of the most important sources of contamination, is responsible for causing several damages to the environment and adversely affecting the health of people. Although the conventional techniques such as precipitation, ion exchange with resins have been extensively used, application of these methods however is not widely practiced because of economical and technical problems. Owing to this it makes indispensable to develop an efficient and very cost effective technology for treatment of heavy metals from aqueous solution.

Recently bio-waste materials from forestry, fishery and agriculture have attracted much attention for separation technology. Therefore numerous approaches have been studied for the development of cheaper and effective metal sorbent, such as fly ash, peat, microbial biomass and agricultural byproduct. In addition, the chemically modified biomass or bio-waste material as biosorbent with surface functional group appears as an alternative technology to offer a technically feasible and economically attractive approach.

The study of the adsorptive action of metallic ions towards the agricultural byproducts may involve metal interactions or coordination to functional groups present in natural protein, lipid and carbohydrate positioned on cell wall.

Cheung *et al.*, [21] studied the adsorption of cadmium and zinc onto Bone char. The equilibrium isotherm were measured and analyzed by using a Langmuir isotherm model. A new film-pore diffusion model was applied to the batch contact time result and good correlations were obtained between theoretical prediction and experimental data. The maximum adsorption capacities were found to be 58.42 mg/g for Cd(II) and 35.15 mg/g for Zn(II).

Sankararamakrishana *et al.*, [3] studied the adsorptive behavior of xanthated chitosan on Cd(II) from tannery wastewater and found that the chemical modification of flake and beads chitosan increased the adsorption capacity. The maximum uptake of cadmium by chemically modified chitosan in batch study was found to be 357.14 mg/g at an optimum pH 8.0, where as for plain chitosan flake it was 85.47 mg/g. Adsorption followed Langmuir isotherm model. Adsorbent-adsorbate kinetics exhibited pseudo second-order model. Desorption of bound cadmium from chemically modified chitosan was accomplished with 0.01N H<sub>2</sub>SO<sub>4</sub>. They also found that, adsorbent even at high concentration of electrolyte, maintains its potential applicability and demonstrated the potential use for other transition metal ions.

Ghimire *et al.*, [10] studied the adsorption of metal ions onto cross linked seaweed, *Laminaria japonica*. The adsorbent exhibited excellent selectivity towards several divalent and trivalent ions. The maximum adsorption capacity for Pb(II), Cd(II) and Fe(III) was found to be 280, 123 and 85.45 mg/g (1.35, 1.1 and 1.53 mol/kg) respectively, and was pH dependent. The experimental data was well fitted according to Langmuir adsorption isotherm. The prepared gel was found to be applicable not only for cationic metal ions but also had shown its potential ability for the adsorption of anionic metal ions by loading the adsorbent gel with Fe(III) prior to its adsorption. Researchers [4] also examined the adsorptive behavior of phosphorylated orange waste loaded with Fe(III) for arsenic removal. The loading capacity for Fe(III) on phosphorylated orange gel was 67.57 mg/g (1.21 mol/kg) higher than on the gel prepared from cellulose 53.61(0.96 mol/kg) and found that arsenic removal efficiency was higher on the phosphorylated orange gel due to higher uptake capacity of gel on Fe(III) which in turn have more ligand exchange capacity. The uptake of Fe(III) was dependent on pH and adsorption was taken place according to Langmuir isotherm and concluded that the adsorbent prepared from seaweed and apple waste revealed to be simple, cost effective and promising for the removal and recovery of metal ions from the aqueous medium.

Reddad *et al.*, [8] studied the efficiency of adsorbent prepared from sugar beet pulp for the removal of Pb(II), Zn(II) and Cd(II) from aqueous solution. They found metal removal was assisted due to numerous carboxylic function of galacturonic acid in the pectin, and this natural adsorbent was able to strongly bind metal cation in aqueous solution. The metal removal was strongly dependent on pH and to a lesser extent to ionic strength. The maximum sorption of Pb(II) and Zn(II) at pH 4 and Cd(II) at pH 6 were 73.76, 17.77, and 24.39 mg/g (0.365, 0.272 and 0.217 mmol g<sup>-1</sup>) respectively.

The use of bio-waste material with surface functional group have been improved selectivity for the removal of heavy metals in water in terms of high efficiency and cost. The prepared adsorbent has been found to be much more efficient than the commercially available activated carbon. Due to this, for the treatment process of water contaminated with heavy metals, biosorption have attracted wide attention in recent years.

Parajuli *et al.*, [9] studied the adsorption behavior of cross linked lignocatechol a modified lignin gel on Pb(II), Fe(III), Cd(II) and Zn(II). They found that adsorption was predominately pH dependent. The optimum pH of the system for Cd(II) and Pb(II) at 5.2 and pH of 2.5 for Fe(III). The Langmuir isotherm was provided the best correlation for the adsorption of the metal ions, from which maximum adsorption capacities were evaluated as 75.39, 129.27 and 370.90 mg/g (1.35, 1.15 and 1.79 mol/kg) for Fe(III), Cd(II) and Pb(II), respectively. The adsorption-elution cycles to check the stability and efficiency of the adsorption gel for the recycling purpose was revealed the feasibility of recycling of the gel. Cation exchange mechanism was postulated as a predominant process of the adsorption.

Hawari *et al.*, [7] investigated the feasibility of anaerobic granules as biosorbent for Pb(II) and Cd(II) removal from aqueous solution. Different ionic forms of anaerobic biomass were evaluated in terms of metal binding capacity. The Ca-biomass was found to have the highest uptake capacity. The solution pH was affected metal uptake. Over the pH-range of 4 -5.5, pH relating effect was not significant. The uptake of was very fast as nearly 75% of the total metal uptake

was completed within the first 5 minutes of contact. The Langmuir isotherm model showed the good fitting, and maximum metal uptake capacity was found to be 255 mg/g for Pb(II) and 60 mg/g for Cd(II).

Abia *et al.*, [12] studied the adsorption of Cd(II), Pb(II) and Zn(II) ions on the Maize cob. Study showed that, the amount of metal ion adsorbed increases with time. The highest sorption rates of the three metal ions were 71% for Zn(II), 132% for Cd(II) and 20% for Pb(II). The study showed the sorption of Zn(II), Cd(II) and Pb(II) ions on the maize cob was particle diffusion controlled.

## 1.6 Objectives of the present study

Numerous approaches have been studied for the development of cheaper and effective metal sorbent in recent years. An alternative technology from agricultural and natural biomass is on progress, which is taken place through biosorption. Since bio-waste material are available almost at the free of cost, is supposed to be more economical with high removal capacity, overall at very low metal concentration to appreciably high.

The main objective of the present study is the systematic evaluation of the performance of a chemically modified xanthated apple waste for the uptake of Pb(II), Cd(II), Zn(II) and Fe(III) from synthetic solution. The specific objectives are as follows:

- To prepare, modify and characterize the adsorbent for heavy metal adsorption from aqueous solution.
- To optimize the experimental condition like, pH.
- To investigate the ability of modified apple waste to remove Pb(II), Cd(II), Zn(II), and Fe(III) separately from aqueous solution.
- To study the kinetic and equilibria of adsorption, determination of sorption isotherm and the influence of competitive cation.

## **1.7 Limitation of the present study**

This study deals with adsorptive behaviour of xanthated apple waste towards Pb(II), Cd(II), Zn(II) and Fe(III) solution prepared in laboratory.

- The only maximum exchangeable cation method has been used for the characterization of adsorbent.
- The adsorption of Pb(II), Cd(II), Zn(II) and Fe(III) has carried out in the pH-range of 1-7 and limited to concentration range of 5- 500 mg/L at laboratory temperature.
- Chemicals available in the laboratory are LR Grade and used directly for their respective concentration determination due to unavailability of certified standard metal ion samples.

## **2. Experimental**

### **2.1 Preparation of the reagent**

#### **2.1.1 0.1 N Nitric Acid**

0.1N nitric acid solution was prepared by mixing 1.6 ml of conc. nitric acid in 1000 ml of volumetric flask in water.

#### **2.1.2 0.1 N Hydrochloric Acid**

1.16 ml of conc. hydrochloric acid was mixed in 1000 ml of volumetric flask in water to prepare 0.1N hydrochloric acid

#### **2.1.3 Stock lead nitrate solution**

Stock solution of 1000 ppm (mg/L) lead nitrate[  $\text{Pb}(\text{NO}_3)_2$ ] was prepared by dissolving 1.598 gm of lead nitrate crystal in a 1000 ml volumetric flask with minimum volume of conc. nitric acid and made up to mark with water.

1000 ml of stock solution of lead nitrate = 1000 mg/L of lead(II)

#### **2.1.4 Stock solution of cadmium nitrate**

2.744 gm of hydrated cadmium nitrate [ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] was dissolved in 1000 ml of volumetric flask with minimum amount of conc. nitric acid and up to mark with water.

1000 ml of stock solution of cadmium nitrate = 1000 mg/L of cadmium(II).

#### **2.1.5 Stock solution of ferric chloride**

2.904 gm of ferric chloride ( $\text{FeCl}_3$ ) was dissolved with conc. hydrochloric acid and filled with water in 1000 ml volumetric flask.

#### **2.1.6 Stock solution of Zinc sulphate**

Stock solution of zinc sulphate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) was prepared by dissolving 4.55 gm of hydrated zinc sulphate with conc. nitric acid in 1000 ml volumetric flask and made up to mark with water.

#### **2.1.7 Working solution of metals**

The working solution of required concentration were prepared by diluting required volume of corresponding metal solution in volumetric flask using water from stock solution of corresponding metal.

### **2.1.8 Sodium hydroxide solution**

0.4 gm of sodium hydroxide was dissolved in 100 ml volumetric flask to make 0.1N and made up to mark with water.

### **2.1.9 Buffer solution**

Buffer solution of pH 4, pH 7 and pH 9 was prepared by dissolving buffer tablets of pH 4, pH 7 and pH 9 in 100 ml volumetric flask in water.

### **2.1.10 Preparation of standard solution**

A series of standard solution of known metal concentration was prepared by appropriate dilution of stock solution of corresponding metal with water containing 0.1N nitric acid.

## **2.2 Preparation of adsorbent**

### **2.2.1 Preparation of adsorbent from apple**

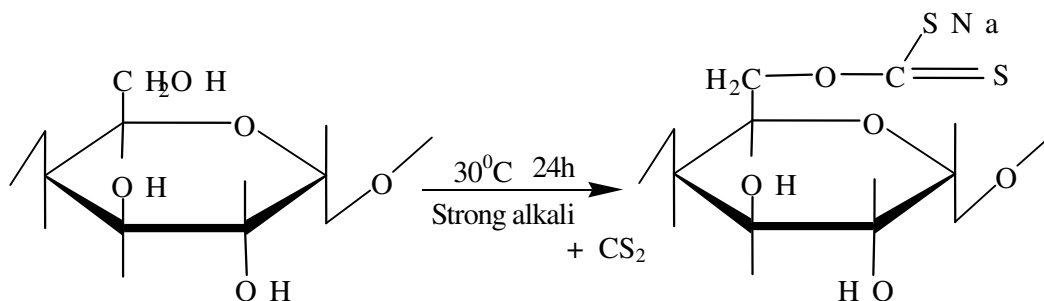
Apple waste after juicing were collected from juice centre and crushed into small size by using juice mixture for about 15 minutes. The crushed apple wastes were dried in an oven for 48 hours at 70°C. The dried wastes were further grounded into small sizes, and used in the present study without any further purification.

### **2.2.2 Modification of adsorbent**

Adsorption performance of adsorbent can be enhanced by modification of raw adsorbent material. Several methods as physical or chemical means can be used for the modification process. The grafting of specific functional groups onto native adsorbent backbone allows its sorption properties to be enhanced and may increase the chemical stability of the sorbent. The correlation between the metal uptake capacity and the amount of xanthate group in biosorbent is related to the number of active surface functional groups occurring in the bio-waste, thus these group can play the predominant role in metal binding.

For the modification, the dried raw apple wastes (20 gm) were treated with 50 ml of 18 % NaOH and shaken for 1h then 10 ml of CS<sub>2</sub> was added and the

mixture was stirred in rotary shaker at room temperature for 24 h. The obtained products were washed with water till neutrality and dried for 24 h at 40°C and sieved to obtain uniform particle size for the experiments. The adsorbent now hereafter called as XAW-gel.



Scheme:1. Plausible reaction for the xanthation process onto monomeric unit of cellulose contained in apple waste.

## 2.3 Adsorption study

### 2.3.1 Batch adsorption study

Batch adsorption experiments were done with synthetic working solution of predetermined concentration and adsorbent prepared from the above procedure. The working solutions of required concentration were prepared from stock solution of corresponding metals. The pH of the working solution were adjusted by using 1M solution of either NaOH or HNO<sub>3</sub> with drop by drop to ensure minimum increase in the solution volume.

The adsorption study were carried out with taking 20 ml of initial working solution of metal of required concentration, 20 mg of adsorbent for each metal in 125 ml stopper bottles and were agitated on a rotary shaker at room temperature for 24 h. At the end of experiment, the sample solution was allowed to settle down and filtered with the help of filter paper. The filtrate metal solutions were



analyzed for its residual concentration from its initial after suitable dilution. The dissolved metal concentrations were assessed by a **Flame atomic absorption (AA) spectrometer** (Perkin Elmer model AAnalyst 100). The pH of the solution before and after of the experiment was adjusted and monitored using **Digital pH meter** (WPA CD 300).

### **2.3.1.1 Effect of pH**

Batch pH studies were examined by shaking 20 ml of each of solution containing approximately 50 mg/L of each of metals with 20mg of gel for 24 h for equilibrium, over a range of initial pH values from 1 to 7 in increment of 1. The samples were shaken in 125 ml stopper bottles with lid. The final pH of the reaction mixture was recorded and samples were used for analyzing the metal ion concentration. The experiments were conducted in triplicate and mean values were used in the analysis of the data. An optimum pH was selected for each metal ion for further studies.

### **2.3.1.2 Effect of initial concentration of metal ions-Adsorption isotherm**

The isotherm studies were conducted at room temperature by varying the initial concentration of each metal solution. Representative approximate concentration (5, 10, 25.....500 mg/L) of metal taking 20 ml were used with 20 mg of gel and agitated for 24 h in shaker. The metal concentrations were determined after filtering the sample. The experiment was repeated for triplicate values. This study helps in evaluating the maximum adsorption capacity of metal ions.

### **2.3.1.3 Effect of shaking time**

The effect of shaking time were studied in separate sets of experiments at optimum pH for each metal taking 100 mg/L metal solution and 20 mg of adsorbent gel and agitated on a shaker at room temperature. The samples were collected at 0.5, 1, 1.5, 2, 3, 4.....and 24 h. The samples were then filtered and

analyzed for each metal ion concentration. For complete uptake under a given condition, the adsorption tests were carried out by shaking 24 h.

#### **2.3.1.4 Effect of binary and tertiary metal adsorption**

The effect of binary and tertiary metal adsorption was carried out by taking initial metal concentration of 50 mg/L of each metal either alone or in combination with the 20 mg of adsorbent gel at the pH range of 1 -6.

#### **2.3.1.5 Kinetic study**

The batch kinetic experiments were conducted at optimum pH for each metal ion by equilibrating 20 mg of adsorbent gel to 125 ml stopper bottles containing 20 ml of metal solution at the concentration levels of 10 mg/L. A separate set of eleven samples were placed on a shaker and shaken vigorously. Samples were filtered through filter paper and the metal ion concentration in the filtrate was analyzed.

### **2.4 Characterization of adsorbent**

#### **2.4.1 Determination of maximum exchangeable cation**

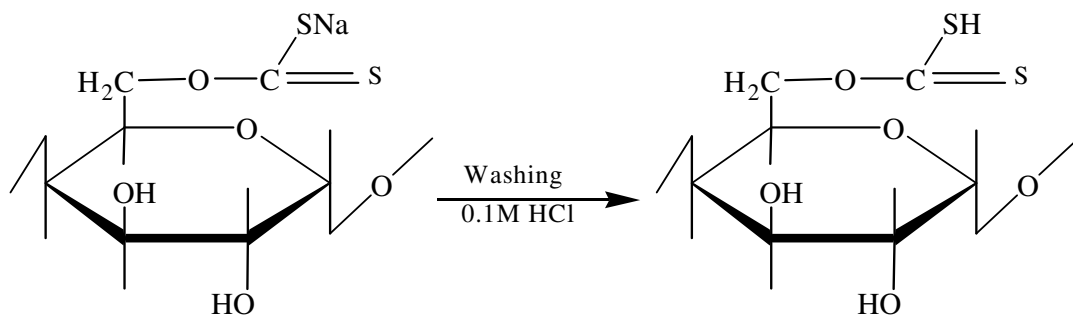
The extent of adsorption depends on the amount of cation that can exchange to other cation. Higher the amount of exchangeable cation (exchangeable functional sites) on adsorbent more will be the amount of uptake of heavy metals. The H<sup>+</sup>-form adsorbent can be used to evaluate the maximum exchangeable cation.

The maximum exchangeable protons were determined through adsorption and subsequent acid-base titration. For the determination, the xanthated material was washed with 0.1M hydrochloric acid solution for 2 h. The suspension was then washed by water till neutrality. The H<sup>+</sup>-gel thus obtained were dried at 70°C for 24 h in electric oven and used to evaluate the maximum exchangeable cation.

Dried H<sup>+</sup>-form gel, 50 mg and 50 ml of 0.01M of sodium hydroxide solution were kept in five 125 ml stopper bottles and equilibrated for 24 h at room temperature. A blank system with deionised water (no base added) and H<sup>+</sup>- gel

was also shaken simultaneously to determine any residual influence of acid onto the XAW-gel. The decrease in basicity in the filtrate was evaluated by titrating the filtrate with 0.01M hydrochloric acid using phenolphthalein as an indicator. All the assays were carried out in triplicate and only mean values are presented.

The total volume of strong acid used during the titration yields the total number of all active surface functional groups for a given mass of biosorbent.



Scheme: 2. Preparation of  $\text{H}^+$ - form gel by washing with dilute hydrochloric solution

### **3 Results and discussions**

#### **3.1 Characterization of adsorbent**

##### **3.1.1 Evaluation of maximum exchangeable cation**

The amount of maximum exchangeable cation contained in H<sup>+</sup>-form gel were evaluated as 2.5 mol/kg. Therefore it can be concluded that, comparatively much cheaper XAW-gel as adsorbent having same functional analog can be used for the removal of heavy metals from aqueous solution.

#### **3.2 Effect of pH**

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the adsorbent, so pH is an important parameter affecting the biosorption of metal ions from aqueous solution. Xanthated apple waste presents a higher content of ionizable groups (xanthate groups mainly from pectin and cellulose) on the cell wall. Which makes it, at least in theory, very liable to the influence of pH. Fig 1 shows the percentage adsorption of Pb(II), Cd(II), Zn(II) and Fe(III) ions as the function of equilibrium pH. The metal uptake by XAW-gel was sensitive to pH variation at the examined range 1 -7. The removal of metal ions by adsorption on XAW-gel was found to increase from 1 to 93 % when the pH was increased from 1 to 7, and thereafter a slight decline in removal was observed with increase in pH. This suggests that, the metal ions are adsorbed according to a cation exchange mechanism. Almost all metal ions are adsorbed at weakly acidic condition.

The optimum pH for the maximum uptake of Fe(III), Pb(II), Zn(II) and Cd(II) onto XAW-gel was found at 3, 4, 5 and 6, respectively. The adsorption increase rapidly near the optimum pH range. However at higher concentration as high as 500 mg/L, the optimum pH was shifted to lower pH value. It was also observed that at the end of the adsorption experiment, pH of the solution increased from lower value to higher. This might be attributed to the protonation of xanthate group and slow release of alkalinity from the prepared sorbent. In case of Fe(III), adsorption decrease rapidly for further increases in pH greater than 3, is probably

due to the precipitation of Fe(III) ions as Fe(OH)<sub>3</sub> precipitate and not due to adsorption. This type of behavior has been observed for other hydrolysable metal also.

The increase or decrease of sorption capacity with the increase of pH may be explained on the basis of surface functional charge of the adsorbent, the degree of ionization and the speciation of the surface functional groups. At low pH, higher concentration of H<sup>+</sup>-ions were present in solution that competes with metal cations for the same functional groups. With increasing pH, the xanthate groups on the adsorbent are unprotonated and tending towards negative, which results in lower electrostatic repulsion and usually higher metal-cation uptakes due to lowered metal solubility. This phenomenon can be confirmed by the observation of sharp increase in final solution pH at optimum pH at which maximum uptake of metal ion has taken place. Additionally for each hydrozable metal ion there is a critical pH range, (often 2 units wide) where the metal uptake efficiency increased from very low level to maximum. Above this range, the solubility of many metal ions in solution decreases enough for precipitation to occur with increasing pH above this range, because it is concerned that, the hydrolyzed species have a lower degree of hydration, that is; less energy is necessary for removal of the hydrated water molecules upon binding [18]. It means, the hydroxyl-metal complexes are strongly adsorbed owing to the formation of an OH group on the metal, which reduces the free energy requirements for adsorption [15]. Therefore, it seems that the adsorption of meal ions can be related to the change in the availability of hydroxyl-metal complexes [M(OH)<sup>n+</sup>].

The order of selectivity with respect to the width of pH range among the tested metal ions is as follows; Pb(II) > Cd(II) > Zn(II) > Fe(III). This facts suggests that feasibility of mutual separation of metals discussed herein themselves by specifying pH values.

### **3.3 Effect of initial concentration of metal ions: Adsorption isotherm**

Figure 2 shows the plot of adsorption isotherm for Pb(II), Cd(II), Zn(II) and Fe(III) on the XAW-gel *i.e.*, the amount of adsorption against the equilibrium

concentration of metal ions and appears that the adsorption of the metal ion increases with the increase in equilibrium metal ion concentration. Uptake is eventually limited by the fixed number of active sites and resulting plateau of isotherm. This is because, at lower metal concentration, the ratio of the initial moles of metal ions to the available surface functional group is low, but at higher concentration, the available functional sites of the sorbent become fewer compared to the moles of metal ions present and hence the uptake of metal becomes independent upon the initial metal ion concentration.

### **3.3.1 Adsorption isotherm model**

Figure 3 and 4 shows the plot of Langmuir and Freundlich isotherm respectively. In both the cases, straight line is obtained. From the plot, the result obtained is also presented in Table 1. It is obvious from the table that, for Pb(II), Cd(II), Zn(II) and Fe(III). The high correlation coefficient for each metal in the case of Langmuir model indicates the favorable condition for adsorption, suggesting the metal ions sorbed to form monolayer coverage on the sorbent surface. The more favorable sorbent is indicated by the higher value of slope of an isotherm. And alternatively from the slope, the maximum adsorption capacity of XAW-gel as a adsorbent were evaluated as 250, 192.30, 123.45 and 62.89 mg/g for Pb(II), Cd(II), Zn(II) and Fe(III), respectively. The biosorbent had shown a preferential binding capacity for heavy metal ions. According to HSAB theory, soft bases tend to form stable complexes with metal such as Cd(II), Pb(II) and Zn(II). Since xanthated groups can be classified as soft bases xanthated polysaccharides, which will have a much higher affinity and sorption capacity than for Fe(III), which itself is classified as hard acid.

**Table: 1- Langmuir and Freundlich biosorption isotherm parameter and correlation coefficient with experimental  $q_{max}$ .**

| Metal   | Langmuir isotherm |           |       | Experimental<br>$q_{max}(mg/g)$ | Freundlich isotherm |       |       |
|---------|-------------------|-----------|-------|---------------------------------|---------------------|-------|-------|
|         | $q_{max}(mg/g)$   | $b(L/mg)$ | $R^2$ |                                 | $K(mg/g)$           | $1/n$ | $R^2$ |
| Pb(II)  | 250.00            | 0.064     | 0.994 | 240                             | 27.49               | 0.44  | 0.950 |
| Cd(II)  | 192.30            | 0.064     | 0.984 | 180                             | 25.11               | 0.38  | 0.963 |
| Zn(II)  | 123.45            | 0.040     | 0.985 | 120                             | 15.84               | 0.33  | 0.925 |
| Fe(III) | 62.89             | 0.032     | 0.997 | 58                              | 4.33                | 0.49  | 0.874 |

### 3.4 Effect of contact time-Kinetic of adsorption

Figure 5 shows the kinetics of metal adsorption onto XAW-gel obtained by batch contact time studies, namely Pb(II), Cd(II), Zn(II) and Fe(III) ions. The plot represents the metal concentration remaining in solution versus time, for an initial metal concentration of 100 mg/g for all metals. It showed that initially sorption were very fast and occurred in two stages *i.e.* initial rapid uptake within 15 -20 min followed by subsequent slow uptake, until steady state condition was attained. The majority of cations were removed within the 30 minutes of contact with the adsorbent. However, the equilibrium times were slightly different among the metals. For Zn(II) and Cd(II) ion, the equilibrium states were reached after 12 h of contact time. In the case of Pb(II) and Fe(III) equilibrium were achieved after 10h and 14h of contact time respectively and no change in the uptake capacity was observed with further increase in equilibrium time upto 24 h. Quantitatively, more Pb(II) ions were adsorbed than Cd(II), than Zn(II) and finally Fe(III) ion.

#### 3.4.1 Modeling of kinetic study

The kinetic study of Pb(II), Cd(II), Zn(II) and Fe(III) adsorption onto XAW-gel were analyzed using linear form of pseudo first-order (Lagergren, 1898) , pseudo second-order (Ho, *et al.*, 1997) and second-order (Lagergren,1898) model. Figure 6, 7 and 8 shows the kinetic plot for pseudo first-order, pseudo second-order and second-order reaction rate. From the plot of each model, the

result obtained for Pb(II), Cd(II), Zn(II) and Fe(III) are also furnished in Table 2. Although all the models adequately described the kinetic data at 95 % confidence level. The plot of 't/q<sub>t</sub>' versus 't' for pseudo second-order reaction kinetic have been shown good straight line than the other model. The Ho's pseudo second-order model best described the kinetic data with higher 'R<sup>2</sup>' value as compared to the Lagergren models for the adsorption of Pb(II), Cd(II), Zn(II) and Fe(III) onto XAW-gel.

The values of predicted equilibrium sorption showed good agreement with the experimental uptake values in the case of pseudo second-order kinetic model and evident that the prepared adsorbent followed pseudo second-order kinetic for the concentration range studied. This is agreed with chemisorptions as the rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate [18].

From comparison of the initial sorption rates  $v_0$  between the metal ions studied, the following tendency concerning hard and soft metal cation were observed: Cd(II) > Zn(II) > Pb(II) > Fe(III). These observations were also in agreement with the work reported earlier with the other metal ion- biomaterial system.

**Table: 2- Kinetic parameter for the metal biosorption with correlation coefficient**

| Metal   | Q <sub>exp</sub><br>mg/g | Pseudo first-order                         |                        |                | Pseudo second-order                           |                        |                |                            | Second-order                                   |                        |                |
|---------|--------------------------|--|------------------------|----------------|---|------------------------|----------------|----------------------------|--|------------------------|----------------|
|         |                          | k <sub>1</sub> x 10 <sup>-3</sup><br>1/min | q <sub>e</sub><br>mg/g | R <sup>2</sup> | k <sub>2</sub> x 10 <sup>-3</sup><br>g/mg.min | q <sub>e</sub><br>mg/g | R <sup>2</sup> | v <sub>0</sub><br>mg/g.min | k <sub>2</sub> ' x 10 <sup>-3</sup><br>g/mgmin | q <sub>e</sub><br>mg/g | R <sup>2</sup> |
| Pb(II)  | 9.92                     | 10.59                                      | 3.63                   | 0.977          | 27.87   | 9.09                   | 0.999          | 1.96                       | 5.10   | 4.54                   | 0.973          |
| Cd(II)  | 9.90                     | 8.29                                       | 2.63                   | 0.973          | 40.00   | 9.09                   | 0.999          | 3.10                       | 4.60   | 3.03                   | 0.989          |
| Zn(II)  | 7.00                     | 10.13                                      | 2.02                   | 0.841          | 52.20   | 6.25                   | 0.999          | 2.03                       | 6.70   | 1.78                   | 0.935          |
| Fe(III) | 6.56                     | 9.44                                       | 1.73                   | 0.925          | 59.52   | 5.00                   | 0.999          | 1.47                       | 8.70   | 1.92                   | 0.979          |



### 3.5 Effect of co-ions

The effect of co-ion on the adsorption behaviour of cadmium, for the applicability in real sense were also studied. The results obtained are given in Table 3. It is obvious from the table that, the cadmium adsorption did not appreciably interfere by other cations like Zn(II), Fe(III), probably due to high formation constant ( $8.0 \times 10^{-27}$ ) of cadmium with xanthate compared to other cations studies.

**Table: 3 - Effect of cations on Cd (II) adsorption.**

| S.N | Cation                  | Amount of Cd(II) adsorbed mg/g |
|-----|-------------------------|--------------------------------|
| 1   | Cd(II)                  | 45.25                          |
| 2   | Cd(II) and Zn(II)       | 42.42                          |
| 3   | Cd(II) and Fe(III)      | 43.72                          |
| 4   | Cd(II), Zn(II), Fe(III) | 42.75                          |

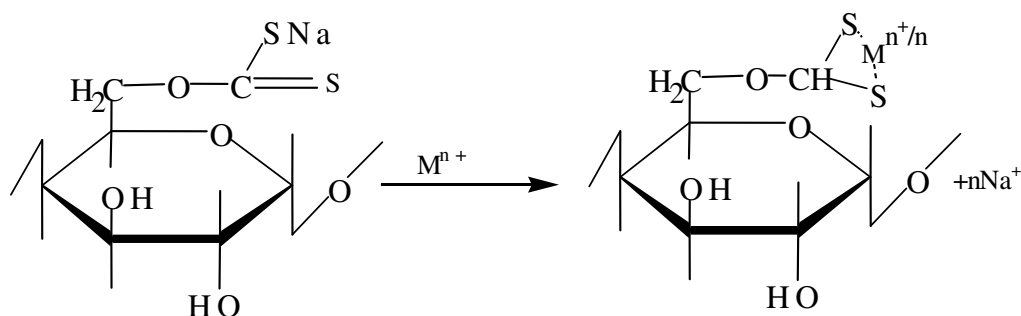
Effect of binary mixture of Pb (II) and Zn(II) adsorption: Separation factor

Figure 9 shows the effect of adsorption for binary mixture of Pb(II) over Zn(II) onto XAW-gel. From the plot it is revealed that Pb(II) can be mutually separated from Zn(II) with a separation factor of 21.

### 3.6 Mechanism of adsorption

The adsorption kinetic study can be highlighted by an ion exchange mechanism responsible for metal uptake process. Since the natural apple waste contains polysaccharides: cellulose along with pectin, containing a number of hydroxyl and carboxyl surface functional groups. In fact the unique mixture of

polysaccharide, mainly cellulose and pectin is largely supposed to be responsible for xanthation which in turn possess excellent metal sequestering ability by creating exchangeable cation sites. Metal adsorption efficiency has to be related to the total number of surface functional group available onto the xanthated gel. As the adsorption behaviour of modified adsorbent was predominantly pH dependent, the probable mechanism between metal ions-xanthated gel interactions could be electrostatic attraction, ion-exchange and/or specific chemical reaction. For example, the divalent and trivalent metal ions are considered to be adsorbed via the formation of stable ring chelates as shown in scheme 3.



Scheme: 3. Inferred adsorption mechanism for ionic species onto monomeric unit of xanthated apple waste according to ligand exchange adsorption

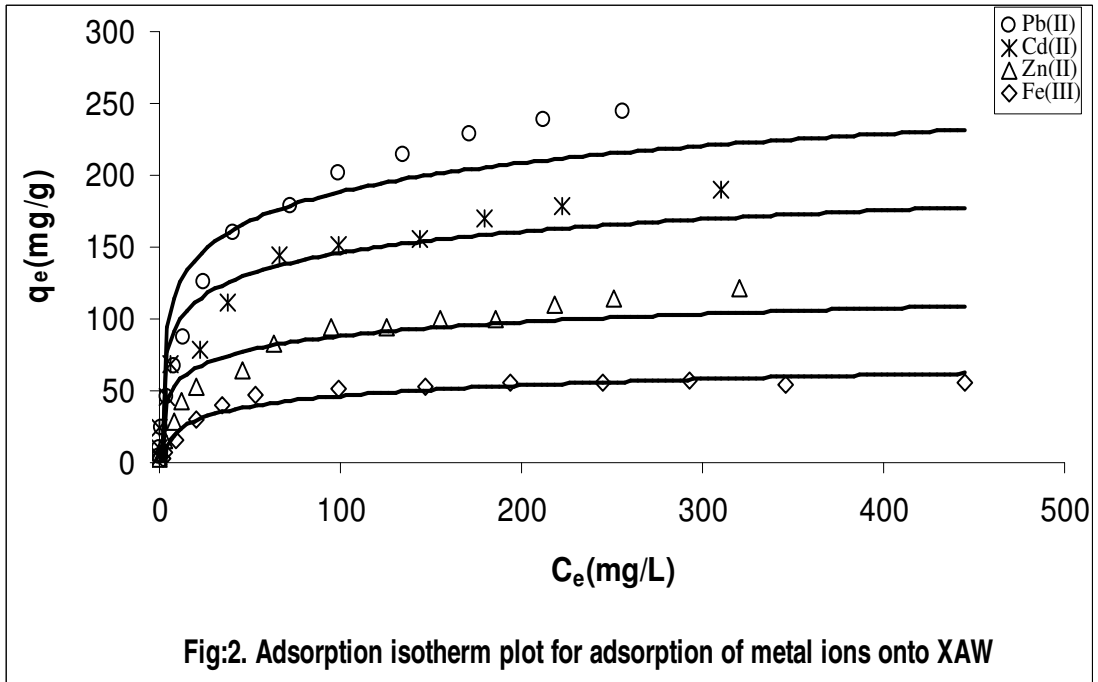
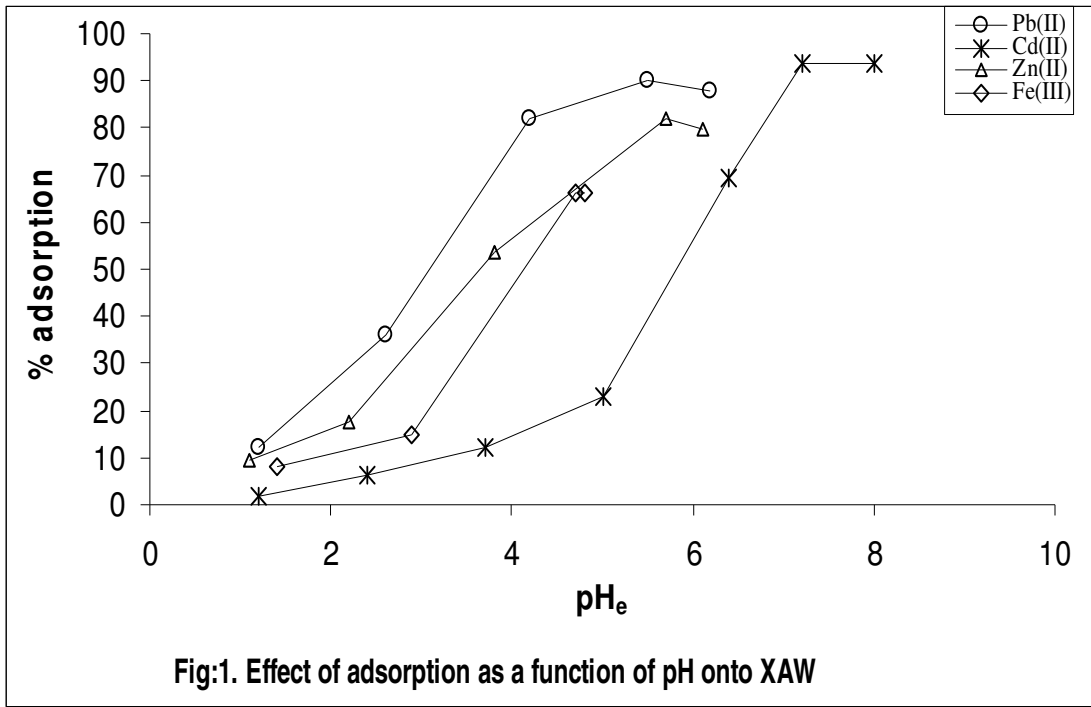
### 3.7 Comparison with other adsorbent

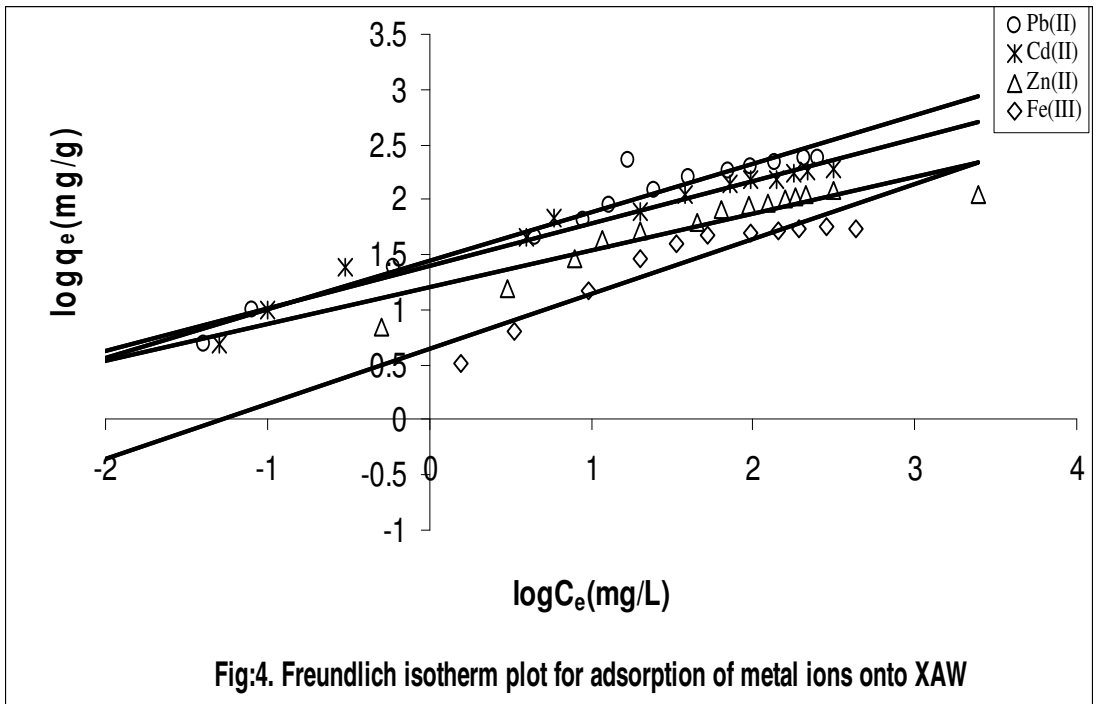
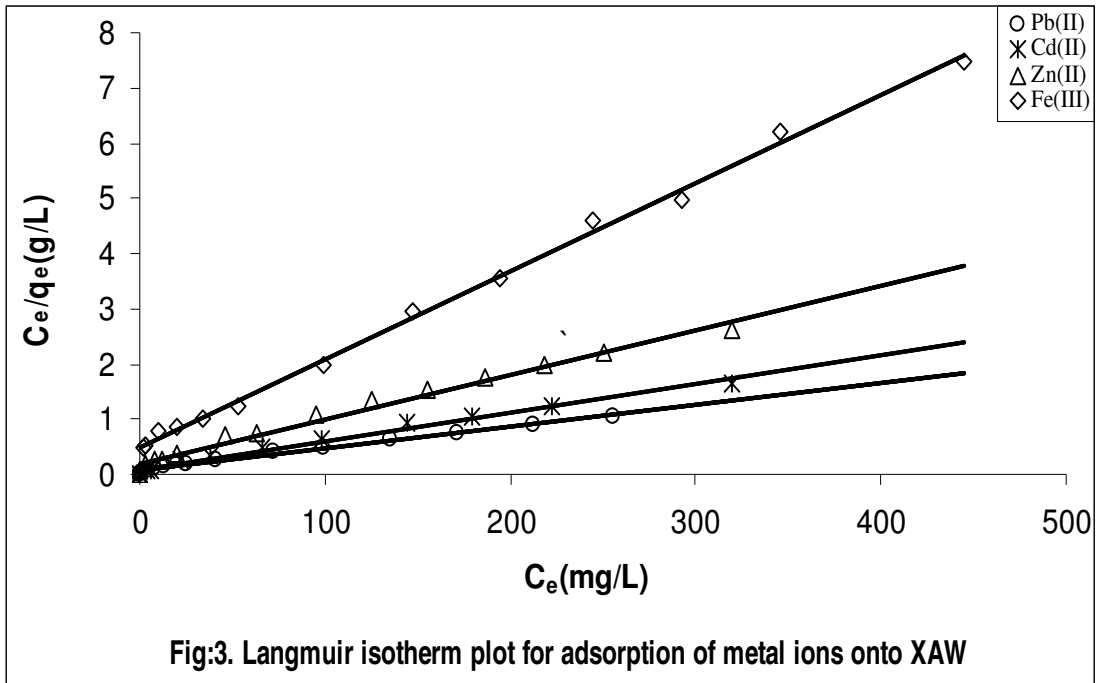
The  $q_m$  values of the modified polysaccharide shown in Table 1 were compared with the metal adsorption capacities reported for other adsorbents, namely activated carbon, agricultural wastes, biomass and some commercial cation exchange resins given in Table 4. More generally, the metal removal capacity of xanthated gel was higher than that of activated carbon, biomasses and

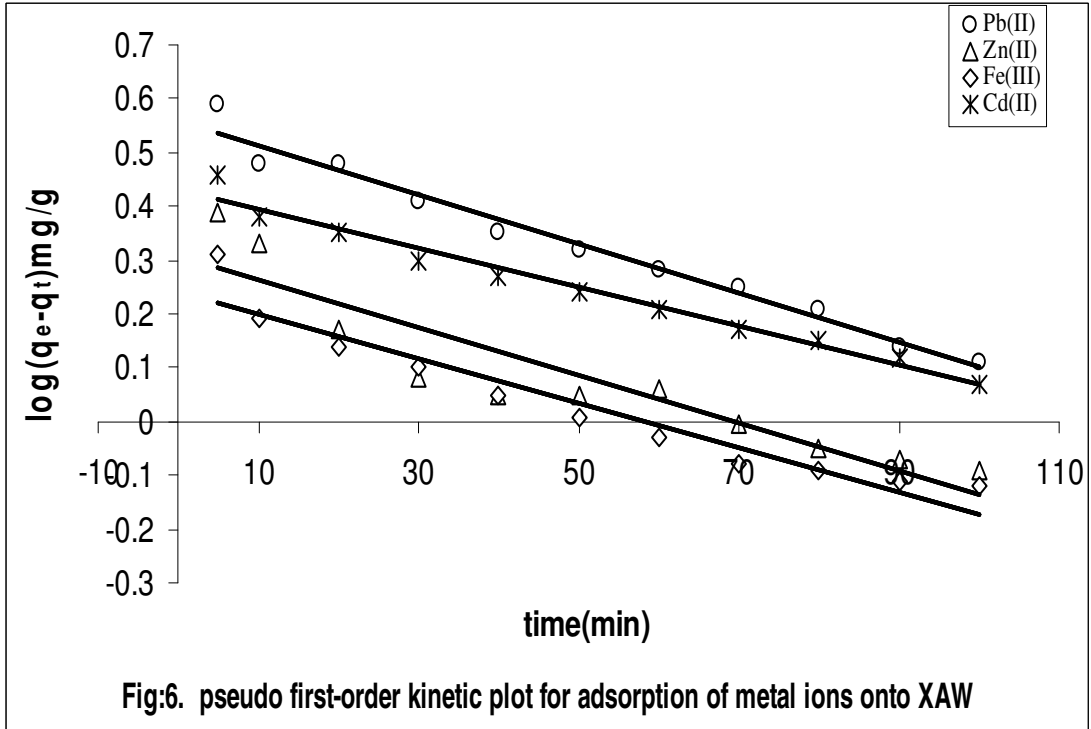
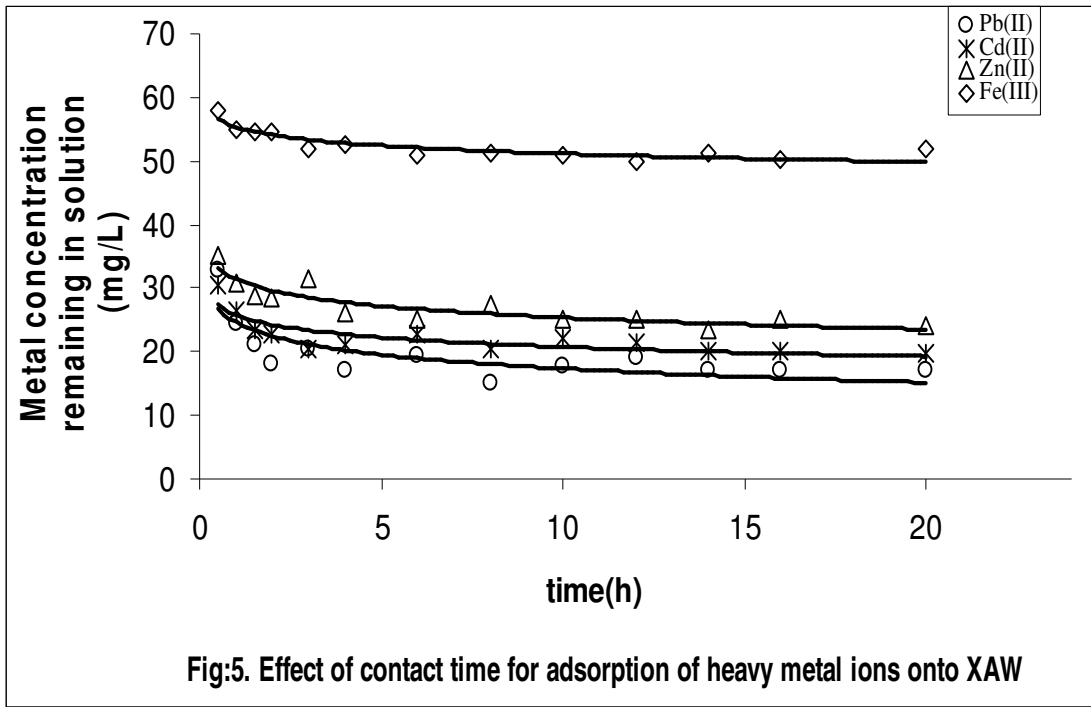
other most of the biosorbent. The metal removal capacity of XAW-gel to some extent observed to be lower than those of some commercial resins, but due to environmentally benign origin produced at low cost, it can be considered as the potential alternative to commercially available synthetic resins.

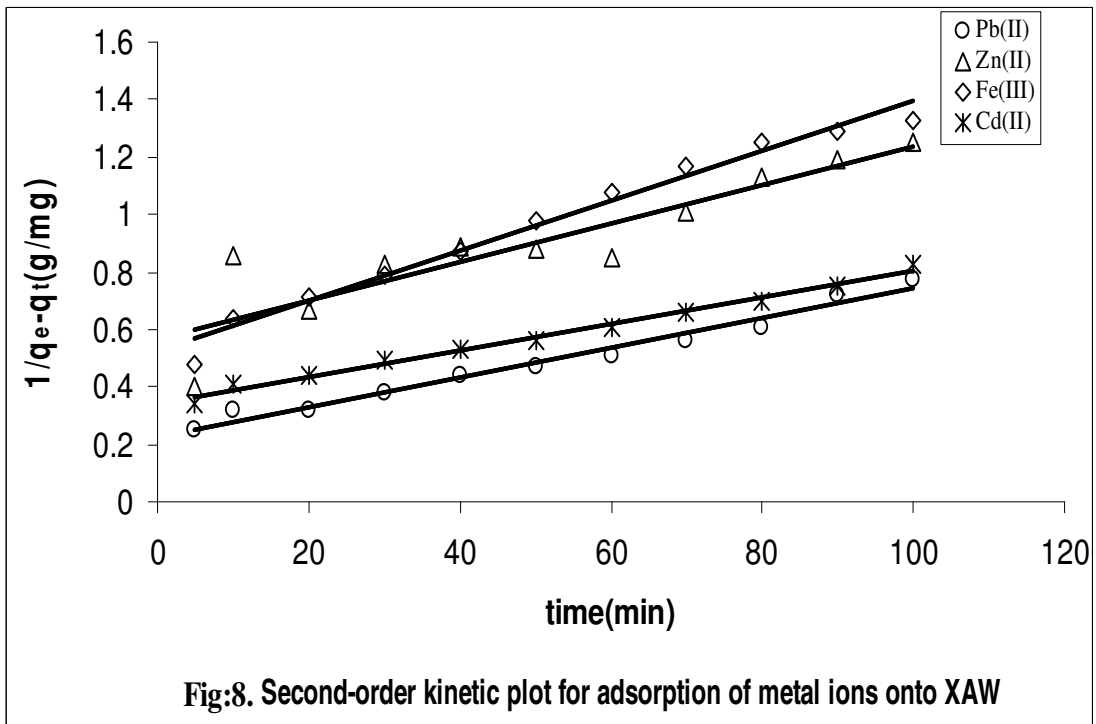
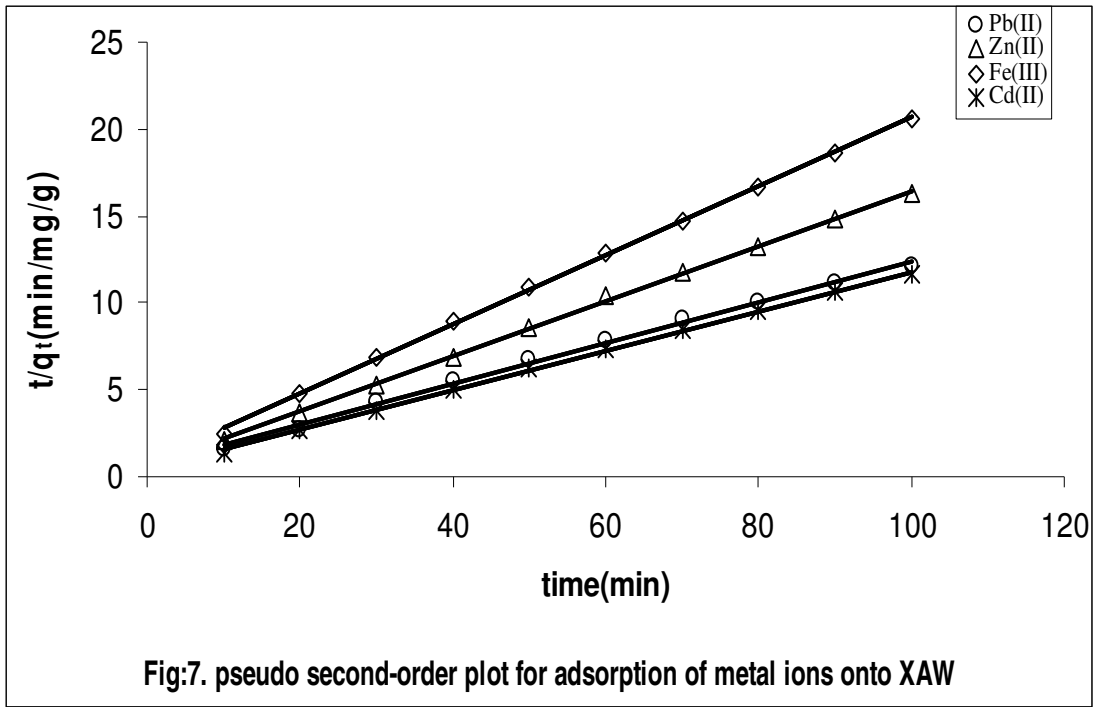
**Table:4.- Comparison of metal adsorption capacities (mg/g) of selected solid wastes, activated carbon and commercial resins.**

| Adsorbent         |                                 | Pb(II) | Cd(II) | Zn(II) | Fe(III) | Condition     | Ref. |
|-------------------|---------------------------------|--------|--------|--------|---------|---------------|------|
| Activated carbon  | Gra. A. C.                      | 16.57  | 3.37   |        |         | pH 5.5        | 7    |
|                   | Powder A.C                      | 26.93  | 3.37   |        |         |               |      |
|                   | A.C fibers                      | 30.45  |        |        |         |               |      |
| Waste sorbents    | Corn cobs                       | 8.28   | 8.98   | 1.96   |         |               | 18   |
|                   | Sugar beet                      | 74     | 24.73  |        |         | 5.5           | 8    |
|                   | Orange waste:<br>Phosphorylated |        |        |        | 67.33   | 3             | 16   |
|                   | Peanut hulls                    | 9.47   | 8.99   | 8.95   |         |               | 8    |
|                   | Raw rice husk                   |        | 8.58   |        |         |               | 26   |
|                   | Nitric acid R. H                |        | 11.03  |        |         | 6             |      |
|                   | Sod. car. R. H                  |        | 16.18  |        |         | 9             |      |
|                   | Sod. hyd. R. H                  |        | 20.24  |        |         |               | 18   |
|                   | Seaweeds:crosslinked            |        |        |        |         |               | 4    |
|                   | <i>P. yezoensis</i>             | 53.87  | 86.55  |        |         |               |      |
|                   | <i>U. japonica</i>              | 59.5   | 30     |        |         |               |      |
|                   | Brown algae:                    |        |        |        |         |               | 5    |
|                   | <i>A. nodosum</i>               | 271.44 | 132.64 |        |         | 3.5           |      |
|                   | <i>S. nataans</i>               | 252.79 | 131.51 |        |         |               |      |
| Maize bran        | 140.85                          |        |        |        |         | 6             | 20   |
| Chitin/chitosan:  |                                 |        |        |        |         | 5             | 3    |
| Chitosan flake    |                                 | 5.93   | 58.83  |        |         |               |      |
| Chitosan beads    |                                 | 250    |        |        |         |               |      |
| Chitin            |                                 | 14.72  |        |        |         |               |      |
| Apple waste:      |                                 |        |        |        |         | Present study |      |
| Xanthated A.W     | 250                             | 192.30 | 123.45 | 62.89  |         |               |      |
| Commercial resins | Duolite GT-73                   | 122.25 | 10.56  | 55.56  |         | 4.8           | 7    |
|                   | Ambrelite IRC- 718              | 290    | 258.5  | 156.8  |         |               |      |
|                   | Ambrelite 200                   | 325.25 | 224.8  | 84.98  |         |               |      |
|                   | Lewalit TP 207                  | 199    | 3.91   | 89.5   |         |               |      |

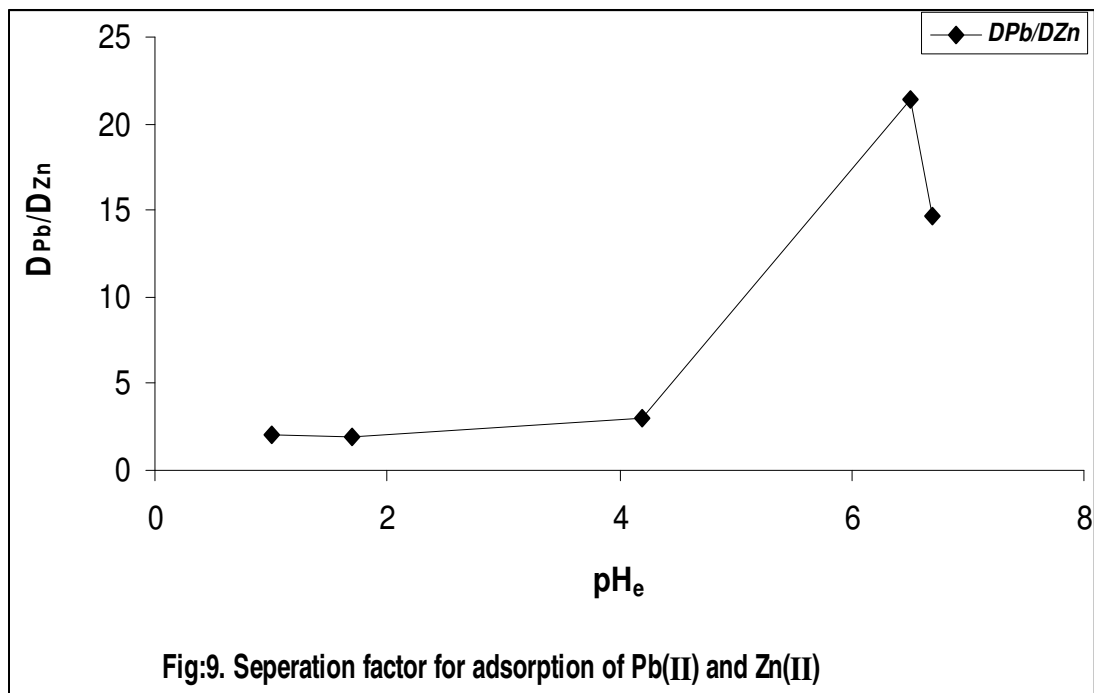












## Conclusion

The use of agricultural byproducts as biosorbent has been offered as an effective way to decrease heavy metal concentration in aqueous medium. Apple (*Pyrus malus*) waste after juicing is a common waste from juice industry, this raw material can be explored as a cation exchanger by simple chemical modification by making reaction with carbon disulphide under alkaline condition. It was characterized and evaluated for its adsorption capacity for Pb(II), Cd(II), Zn(II) and Fe(III) ions. The maximum amounts of exchangeable cations contained in the H<sup>+</sup>-gel evaluated were 2.52 mol/kg.

The metal sorption depended on solution pH, initial concentration of adsorbate, contact time and presence of other cation in the system. The pH of the solution has shown to be one of the key variables for metal ions removal. The optimum pH for Pb(II) and Zn(II) was observed at 4 while that for Fe(III) and Cd(II) was found to be 3 and 6, respectively. The adsorption data pertaining for equilibrium process was in good agreement with Langmuir adsorption isotherm, from which the maximum uptake of Pb(II), Cd(II), Zn(II) and Fe(III) evaluated was 250, 192.30, 123.45 and 62.89 mg/g, respectively, with the order of Pb(II) > Cd(II) > Zn(II) > Fe(III). Both experimental and Langmuir isotherm is in well agreement for the maximum adsorption by the native adsorbent. The predominant ion exchange mechanism is supposed to be involving between the cation containing with sulphur at xanthate group. The pseudo second-order kinetic model provided the best correlation for the experimental data obtained, compared to Lagergren kinetic model. Due to high stability constant of cadmium with xanthate group, interference from cation under study did not found

Although the metal adsorption capacity are, to some extent, lower than those of synthetic resin, the xanthated apple waste as adsorbent possessed higher metal uptake capacity as compared to several other materials. Thus the adsorbent investigated from this study provided an attractive adsorbent at low cost with excellent selectivity even at high concentration of electrolyte, so it could be a potential alternative for the removal/separation of heavy metals from natural and industrial wastewater.

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# Appendix

**Table: 5. Effect of pH for adsorption of Pb(II) onto XAW.**

Total volume - 20 ml

Amount of adsorbent - 20 mg

| S.N | Initial pH | Equilibrium pH | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | % adsorption |
|-----|------------|----------------|------------------------------------|--|--------------|
| 1   | 1          | 1.2            | 50                                 | 44                                     | 12           |
| 2   | 2          | 2.6            | 50                                 | 34                                     | 36           |
| 3   | 3          | 4.2            | 50                                 | 9                                      | 82           |
| 4   | 4          | 5.5            | 50                                 | 5                                      | 90           |
| 5   | 5          | 6.2            | 50                                 | 6                                      | 88           |

**Table: 6. Adsorption isotherm for adsorption of Pb(II) onto XAW.**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

pH - 4

| S.N | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | Amount of Pb(II) adsorbed $q_e$ (mg/g) | $C_e/q_e$ (L/g) | $\log C_e$ (mg/L) | $\log q_e$ (mg/g) |
|-----|------------------------------------|--|--|-----------------|-------------------|-------------------|
| 1   | 5.00                               | 0.04                                   | 4.96                                   | 0.008           | -1.39             | 0.69              |
| 2   | 10.00                              | 0.08                                   | 9.92                                   | 0.008           | -1.09             | 0.99              |
| 3   | 25.00                              | 0.60                                   | 24.40                                  | 0.02            | -0.22             | 1.38              |
| 4   | 50.00                              | 4.52                                   | 45.48                                  | 0.08            | 0.65              | 1.65              |
| 5   | 75.00                              | 7.86                                   | 67.14                                  | 0.11            | 0.95              | 1.82              |
| 6   | 100.00                             | 12.91                                  | 87.10                                  | 0.14            | 1.11              | 1.94              |
| 7   | 150.00                             | 24.70                                  | 125.30                                 | 0.19            | 1.39              | 2.09              |
| 8   | 200.00                             | 40.65                                  | 159.35                                 | 0.25            | 1.60              | 2.20              |
| 9   | 250.00                             | 72.00                                  | 178.00                                 | 0.40            | 1.85              | 2.25              |
| 10  | 300.00                             | 99.00                                  | 201.00                                 | 0.49            | 1.99              | 2.30              |
| 11  | 350.00                             | 135.00                                 | 215.00                                 | 0.62            | 2.13              | 2.33              |
| 12  | 400.00                             | 171.00                                 | 229.00                                 | 0.74            | 2.23              | 2.35              |
| 13  | 450.00                             | 212.00                                 | 238.00                                 | 0.89            | 2.32              | 2.37              |
| 14  | 500.00                             | 256.00                                 | 244.00                                 | 1.05            | 2.40              | 2.38              |

**Table: 7. Effect of pH for adsorption of Cd(II) onto XAW.**

Total volume - 20 ml

Amount of adsorbent - 20 mg

| S.N | Initial pH | Equilibrium pH | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | % adsorption |
|-----|------------|----------------|------------------------------------|--|--------------|
| 1   | 1          | 1.2            | 50                                 | 48.98                                  | 2.01         |
| 2   | 2          | 2.4            | 50                                 | 46.90                                  | 6.20         |
| 3   | 3          | 3.7            | 50                                 | 44.00                                  | 12.00        |
| 4   | 4          | 5.0            | 50                                 | 38.55                                  | 22.90        |
| 5   | 5          | 6.4            | 50                                 | 15.21                                  | 69.58        |
| 6   | 6          | 7.2            | 50                                 | 3.15                                   | 93.70        |
| 7   | 7          | 8.0            | 50                                 | 3.20                                   | 93.60        |

**Table: 8. Adsorption isotherm for adsorption of Cd(II) onto XAW.**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

pH - 6

| S.N | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | Amount of Cd(II) adsorbed $q_e$ (mg/g) | $C_e/q_e$ (L/g) | $\log C_e$ (mg/L) | $\log q_e$ (mg/g) |
|-----|------------------------------------|--|--|-----------------|-------------------|-------------------|
| 1   | 5.00                               | 0.05                                   | 4.95                                   | 0.01            | -1.30             | 0.69              |
| 2   | 10.00                              | 0.10                                   | 9.90                                   | 0.01            | -1.00             | 0.99              |
| 3   | 25.00                              | 0.30                                   | 24.70                                  | 0.01            | -0.52             | 1.39              |
| 4   | 50.00                              | 4.00                                   | 46.00                                  | 0.08            | 0.60              | 1.66              |
| 5   | 75.00                              | 6.00                                   | 69.00                                  | 0.08            | 0.77              | 1.83              |
| 6   | 100.00                             | 22.00                                  | 78.00                                  | 0.25            | 1.30              | 1.89              |
| 7   | 150.00                             | 38.00                                  | 112.00                                 | 0.34            | 1.58              | 2.05              |
| 8   | 200.00                             | 66.00                                  | 144.00                                 | 0.49            | 1.86              | 2.15              |
| 9   | 250.00                             | 98.58                                  | 151.42                                 | 0.65            | 1.99              | 2.18              |
| 10  | 300.00                             | 144.00                                 | 156.00                                 | 0.92            | 2.15              | 2.19              |
| 11  | 350.00                             | 179.36                                 | 170.64                                 | 1.05            | 2.25              | 2.23              |
| 12  | 400.00                             | 222.00                                 | 178.00                                 | 1.24            | 2.34              | 2.25              |
| 13  | 500.00                             | 310.00                                 | 190.00                                 | 1.63            | 2.50              | 2.27              |

**Table: 9. Effect of pH for adsorption of Zn(II) onto XAW.**

Total volume - 20 ml

Amount of adsorbent - 20 mg

| S.N | Initial pH | Equilibrium pH | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | % adsorption |
|-----|------------|----------------|------------------------------------|--|--------------|
| 1   | 1          | 1.1            | 50                                 | 45.22                                  | 9.56         |
| 2   | 2          | 2.2            | 50                                 | 41.24                                  | 17.52        |
| 3   | 3          | 3.8            | 50                                 | 23.18                                  | 53.64        |
| 4   | 4          | 5.7            | 50                                 | 9.08                                   | 81.84        |
| 5   | 5          | 6.1            | 50                                 | 10.02                                  | 79.78        |

**Table: 10. Adsorption isotherm for adsorption of Zn(II) onto XAW.**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

pH - 4

| S.N | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | Amount of Zn(II) adsorbed $q_e$ (mg/g) | $C_e/q_e$ (L/g) | $\log C_e$ (mg/L) | $\log q_e$ (mg/g) |
|-----|------------------------------------|--|--|-----------------|-------------------|-------------------|
| 1   | 3.70                               | 0.02                                   | 3.50                                   | 0.005           | -2.24             | 0.54              |
| 2   | 7.50                               | 0.50                                   | 7                                      | 0.07            | -0.30             | 0.84              |
| 3   | 18.70                              | 3                                      | 16                                     | 0.18            | 0.48              | 1.20              |
| 4   | 37.00                              | 8                                      | 29                                     | 0.27            | 0.90              | 1.46              |
| 5   | 55.00                              | 12                                     | 43                                     | 0.28            | 1.07              | 1.63              |
| 6   | 79.00                              | 20                                     | 53                                     | 0.37            | 1.30              | 1.7               |
| 7   | 109.50                             | 46                                     | 64                                     | 0.71            | 1.66              | 1.80              |
| 8   | 146.00                             | 63                                     | 83                                     | 0.75            | 1.80              | 1.91              |
| 9   | 182.00                             | 95                                     | 95                                     | 1.08            | 1.98              | 1.94              |
| 10  | 219.00                             | 125                                    | 94                                     | 1.33            | 2.09              | 1.97              |
| 11  | 255.00                             | 155                                    | 100                                    | 1.55            | 2.20              | 2.00              |
| 12  | 292.00                             | 186                                    | 106                                    | 1.75            | 2.26              | 2.02              |
| 13  | 328.00                             | 218                                    | 110                                    | 1.98            | 2.33              | 2.04              |
| 14  | 365.00                             | 251                                    | 114                                    | 2.20            | 2.39              | 2.05              |
| 15  | 438.00                             | 320                                    | 122                                    | 2.61            | 2.50              | 2.08              |



**Table: 11. Effect of pH for adsorption of Fe(III) onto XAW.**

Total volume - 20 ml

Amount of adsorbent - 20 mg

| S.N | Initial pH | Equilibrium pH | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | % adsorption |
|-----|------------|----------------|------------------------------------|--|--------------|
| 1   | 1          | 1.4            | 50                                 | 46                                     | 8            |
| 2   | 2          | 2.9            | 50                                 | 42.59                                  | 14.82        |
| 3   | 3          | 4.7            | 50                                 | 16.88                                  | 66.24        |
| 4   | 4          | 5              | 50                                 | 17                                     | 66           |

**Table: 12. Adsorption isotherm for adsorption of Fe(III) onto XAW.**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

pH - 3

| S.N | Initial concentration $C_i$ (mg/L) | Equilibrium concentration $C_e$ (mg/L) | Amount of Fe(III) adsorbed $q_e$ (mg/g) | $C_e/q_e$ (L/g) | $\log C_e$ (mg/L) | $\log q_e$ (mg/g) |
|-----|------------------------------------|--|---|-----------------|-------------------|-------------------|
| 1   | 5.00                               | 1.62                                   | 3.38                                    | 0.48            | 0.20              | 0.52              |
| 2   | 10.00                              | 3.44                                   | 6.57                                    | 0.52            | 0.53              | 0.81              |
| 3   | 25.00                              | 5.59                                   | 15.41                                   | 0.62            | 0.98              | 1.18              |
| 4   | 50.00                              | 20.27                                  | 29.73                                   | 0.68            | 1.30              | 1.47              |
| 5   | 75.00                              | 34.40                                  | 40.60                                   | 0.84            | 1.53              | 1.60              |
| 6   | 100.00                             | 52.68                                  | 47.32                                   | 1.11            | 1.72              | 1.67              |
| 7   | 150.00                             | 99.00                                  | 51.00                                   | 1.94            | 1.99              | 1.70              |
| 8   | 200.00                             | 147.00                                 | 53.00                                   | 2.77            | 2.16              | 1.72              |
| 9   | 250.00                             | 194.00                                 | 56.00                                   | 3.46            | 2.28              | 1.74              |
| 10  | 300.00                             | 244.79                                 | 55.21                                   | 4.43            | 2.38              | 1.74              |
| 11  | 350.00                             | 292.75                                 | 57.25                                   | 5.11            | 2.46              | 1.75              |
| 12  | 400.00                             | 345.55                                 | 54.45                                   | 6.34            | 2.53              | 1.73              |
| 13  | 500.00                             | 444.67                                 | 55.33                                   | 8.03            | 2.64              | 1.74              |

**Table: 13. Effect of contact time for adsorption of metal ions onto XAW.**

Total volume (V) - 20 ml.

Amount of adsorbent (W) - 20 mg.

Initial metal ion concentration - 100 mg/L

| S.N | Time (h) | Pb(II)<br>Equ <sup>m</sup> .<br>conc.(mg/L) | Cd(II)<br>Equ <sup>m</sup> . conc.<br>(mg/L) | Zn(II)<br>Equ <sup>m</sup> . conc.<br>(mg/L) | Fe(III)<br>Equ <sup>m</sup> . conc.<br>(mg/L) |
|-----|----------|---|--|--|---|
| 1   | 0.5      | 32.92                                       | 30.42  | 35.25  | 58.00   |
| 2   | 1        | 24.47                                       | 26.60  | 30.73  | 55.02   |
| 3   | 1.5      | 20.98                                       | 23.34  | 28.64  | 54.71   |
| 4   | 2        | 18.24                                       | 22.02  | 28.54  | 54.50   |
| 5   | 3        | 20.57                                       | 20.32  | 31.45  | 52.00   |
| 6   | 4        | 17.17                                       | 21.00  | 26.21  | 52.54   |
| 7   | 5        | 18.22                                       | 24.08  | 27.00  | 49.16   |
| 8   | 6        | 19.48                                       | 22.80  | 25.17  | 51.00   |
| 9   | 8        | 18.08                                       | 21.84  | 27.89  | 53.41   |
| 10  | 10       | 15.92                                       | 20.53  | 27.45  | 51.08   |
| 11  | 12       | 16.60                                       | 18.42  | 26.08  | 50.44   |
| 12  | 14       | 17.77                                       | 22..00                                       | 25.02  | 50.82   |
| 13  | 16       | 20.70                                       | 21.63  | 25.21  | 51.52   |
| 14  | 18       | 19.10                                       | 21.54  | 25.15  | 50.00   |
| 15  | 20       | 17.09                                       | 21.20  | 24.23  | 47.49   |
| 16  | 22       | 17.08                                       | 20.23  | 23.41  | 51.21   |
| 17  | 24       | 17.12                                       | 20.30  | 25.40  | 52.24   |

**Table: 14. Kinetic data for adsorption of Pb(II) onto XAW**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

Initial metal concentration( $C_i$ ) - 10 mg/L

pH - 4

| S.N | Time (min) | Equ <sup>m</sup> conc. $C_e$ (mg/L) | $q_t$ (mg/g) | $t/q_t$ (min/mg/g) | $q_e - q_t$ (mg/g) | $1/q_e - q_t$ (g/mg) | $\log(q_e - q_t)$ mg/g |
|-----|------------|-------------------------------------|--------------|--------------------|--------------------|----------------------|------------------------|
| 1   | 5          | 4.40                                | 5.61         | 0.89               | 3.93               | 0.25                 | 0.59                   |
| 2   | 10         | 3.52                                | 6.49         | 1.54               | 3.05               | 0.32                 | 0.48                   |
| 3   | 20         | 3.28                                | 6.49         | 2.67               | 3.05               | 0.32                 | 0.48                   |
| 4   | 30         | 3.06                                | 6.94         | 4.32               | 2.60               | 0.38                 | 0.41                   |
| 5   | 40         | 2.84                                | 7.29         | 5.48               | 2.25               | 0.44                 | 0.35                   |
| 6   | 50         | 2.64                                | 7.44         | 6.72               | 2.10               | 0.47                 | 0.32                   |
| 7   | 60         | 2.40                                | 7.60         | 7.89               | 1.94               | 0.51                 | 0.28                   |
| 8   | 70         | 2.24                                | 7.76         | 9.02               | 1.78               | 0.56                 | 0.25                   |
| 9   | 80         | 2.08                                | 7.92         | 10.01              | 1.62               | 0.61                 | 0.21                   |
| 10  | 90         | 1.84                                | 8.16         | 11.11              | 1.38               | 0.72                 | 0.14                   |
| 11  | 100        | 1.60                                | 8.25         | 12.12              | 1.29               | 0.77                 | 0.11                   |
| 12  | 24h        | 0.46                                | 9.54         |                    |                    |                      |                        |

**Table: 15. Kinetic data for adsorption of Cd(II) onto XAW**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

Initial metal concentration( $C_i$ ) - 10 mg/L

pH - 6

| S.N | Time<br>(min) | Equ <sup>m</sup><br>conc.<br>$C_e$ (mg/L) | $q_t$<br>(mg/g) | $t/q_t$<br>(min/mg/g) | $q_e - q_t$<br>(mg/g) | $1/q_e - q_t$<br>(g/mg) | $\log (q_e - q_t)$<br>mg/g |
|-----|---------------|---|-----------------|-----------------------|-----------------------|-------------------------|----------------------------|
| 1   | 5             | 3.30                                      | 6.88            | 0.72                  | 2.92                  | 0.34                    | 0.46                       |
| 2   | 10            | 2.90                                      | 7.37            | 1.35                  | 2.43                  | 0.41                    | 0.38                       |
| 3   | 20            | 2.70                                      | 7.56            | 2.64                  | 2.24                  | 0.44                    | 0.35                       |
| 4   | 30            | 2.50                                      | 7.77            | 3.86                  | 2.03                  | 0.49                    | 0.30                       |
| 5   | 40            | 2.45                                      | 7.93            | 5.04                  | 1.87                  | 0.53                    | 0.27                       |
| 6   | 50            | 2.35                                      | 8.03            | 6.22                  | 1.77                  | 0.56                    | 0.24                       |
| 7   | 60            | 2.20                                      | 8.17            | 7.34                  | 1.63                  | 0.61                    | 0.21                       |
| 8   | 70            | 2.10                                      | 8.30            | 8.43                  | 1.50                  | 0.66                    | 0.17                       |
| 9   | 80            | 2.02                                      | 8.38            | 9.54                  | 1.42                  | 0.70                    | 0.15                       |
| 10  | 90            | 1.92                                      | 8.48            | 10.61                 | 1.32                  | 0.75                    | 0.12                       |
| 11  | 100           | 1.80                                      | 8.60            | 11.62                 | 1.20                  | 0.83                    | 0.08                       |
| 12  | 24h           | 0.20                                      | 9.80            |                       |                       |                         |                            |

**Table: 16. Kinetic data for adsorption of Zn(II) onto XAW**

Total volume - 20 ml.

Amount of adsorbent - 20 mg.

Initial metal concentration( $C_i$ ) - 10 mg/L

pH - 4

| S.N | Time<br>(min) | Equ <sup>m</sup><br>conc.<br>$C_e$ (mg/L) | $q_t$<br>(mg/g) | $t/q_t$<br>(min/mg/g) | $q_e - q_t$<br>(mg/g) | $1/q_e - q_t$<br>(g/mg) | $\log (q_e - q_t)$<br>mg/g |
|-----|---------------|---|-----------------|-----------------------|-----------------------|-------------------------|----------------------------|
| 1   | 5             | 5.54                                      | 4.46            | 1.12                  | 2.46                  | 0.40                    | 0.39                       |
| 2   | 10            | 5.24                                      | 4.76            | 2.10                  | 1.16                  | 0.86                    | 0.33                       |
| 3   | 20            | 4.42                                      | 5.58            | 3.68                  | 1.49                  | 0.67                    | 0.17                       |
| 4   | 30            | 4.28                                      | 5.72            | 5.24                  | 1.20                  | 0.83                    | 0.08                       |
| 5   | 40            | 4.20                                      | 5.80            | 6.89                  | 1.12                  | 0.89                    | 0.05                       |
| 6   | 50            | 4.21                                      | 5.79            | 8.63                  | 1.13                  | 0.88                    | 0.05                       |
| 7   | 60            | 4.25                                      | 5.75            | 10.42                 | 1.17                  | 0.85                    | 0.06                       |
| 8   | 70            | 4.07                                      | 5.93            | 11.80                 | 0.99                  | 1.01                    | -0.004                     |
| 9   | 80            | 3.96                                      | 6.04            | 13.24                 | 0.88                  | 1.13                    | -0.05                      |
| 10  | 90            | 3.92                                      | 6.08            | 14.80                 | 0.84                  | 1.19                    | -0.07                      |
| 11  | 100           | 3.88                                      | 6.12            | 16.33                 | 0.80                  | 1.25                    | -0.09                      |
| 12  | 24h           | 3.08                                      | 6.92            |                       |                       |                         |                            |

**Table: 17. Kinetic data for adsorption of Fe(III) onto XAW**

Total volume (V) - 20 ml.

Amount of adsorbent (W) - 20 mg.

Initial metal concentration (C<sub>i</sub>) - 10 mg/L

pH - 3

| S.N | Time<br>(min) | Equ <sup>m</sup><br>conc.<br>C <sub>e</sub> (mg/L) | q <sub>t</sub><br>(mg/g) | t/q <sub>t</sub><br>(min/mg/g) | q <sub>e</sub> -q <sub>t</sub><br>(mg/g) | 1/q <sub>e</sub> -q <sub>t</sub><br>(g/mg) | log (q <sub>e</sub> -q <sub>t</sub> )<br>mg/g |
|-----|---------------|--|--------------------------|--------------------------------|--|--|---|
| 1   | 5             | 6.45   | 3.55                     | 1.40                           | 2.05                                     | 0.48                                       | 0.31  |
| 2   | 10            | 5.95   | 4.05                     | 2.46                           | 1.55                                     | 0.64                                       | 0.19  |
| 3   | 20            | 5.80   | 4.20                     | 4.76                           | 1.40                                     | 0.71                                       | 0.14  |
| 4   | 30            | 5.66   | 4.34                     | 6.91                           | 1.26                                     | 0.79                                       | 0.10  |
| 5   | 40            | 5.54   | 4.46                     | 8.96                           | 1.14                                     | 0.87                                       | 0.05  |
| 6   | 50            | 5.42   | 4.58                     | 10.91                          | 1.02                                     | 0.98                                       | 0.008   |
| 7   | 60            | 5.32   | 4.68                     | 12.82                          | 0.92                                     | 1.08                                       | -0.03   |
| 8   | 70            | 5.25   | 4.75                     | 14.73                          | 0.85                                     | 1.17                                       | -0.08   |
| 9   | 80            | 5.20   | 4.80                     | 16.66                          | 0.80                                     | 1.25                                       | -0.09   |
| 10  | 90            | 5.17   | 4.83                     | 18.63                          | 0.77                                     | 1.29                                       | -0.11   |
| 11  | 100           | 5.15   | 4.85                     | 20.61                          | 0.75                                     | 1.33                                       | -0.12   |
| 12  | 24h           | 4.40   | 5.60                     |                                |  |  |   |

**Table: 18. Separation factor for adsorption of Pb(II) and Zn(II) onto XAW**

Volume taken - 20 ml.

Amount of adsorbent - 20 gm.

Initial concentration - 50 mg/L

| S. N | Initial pH | Equ <sup>m</sup> pH | Pb(II)                |                       |  | Zn(II)                |                       |  | $\frac{D_{Pb}}{D_{Zn}}$ |
|------|------------|---------------------|-----------------------|-----------------------|--|-----------------------|-----------------------|--|-------------------------|
|      |            |                     | C <sub>e</sub> (mg/L) | q <sub>e</sub> (mg/g) | D = q <sub>e</sub> /C <sub>e</sub> (L/g) | C <sub>e</sub> (mg/L) | q <sub>e</sub> (mg/g) | D = q <sub>e</sub> /C <sub>e</sub> (L/g) |                         |
| 1    | 1          | 1                   | 46                    | 4                     | 0.08                                     | 48                    | 2                     | 0.04                                     | 2                       |
| 2    | 2          | 1.7                 | 40                    | 10                    | 0.25                                     | 44                    | 6                     | 0.13                                     | 1.9                     |
| 3    | 3          | 4.2                 | 22                    | 28                    | 1.27                                     | 35                    | 15                    | 0.42                                     | 3.02                    |
| 4    | 4          | 6.5                 | 5                     | 45                    | 9.00                                     | 35                    | 15                    | 0.42                                     | 21.42                   |
| 5    | 5          | 6.8                 | 9                     | 41                    | 4.55                                     | 38                    | 12                    | 0.31                                     | 14.67                   |