1. INTRODUCTION

1.1. GENERAL INTRODUCTION

Heavy metals have become the major surface water and ground water contaminants. They are discharged by various industries such as electroplating, metal finishing, textile, mining and agricultural activities. The presence and persistence of certain heavy metals in the environment is the burning problem of the today's world.[1] The release of heavy metals such as Ni^{2+}, Pb^{2+}, Hg^{2+} etc into the environment is a potential threat to water and soil quality as well as to animal and human health. Unlike organic pollutants heavy metals don't degrade into less harmful substances and can accumulate in soil and water reservoirs which lead to the harmful effects on living species if they enter into the food chain.[1]

Conventional method for heavy metal removal from aqueous solution includes chelation, solvent extraction and liquid membrane separation. Application of these methods, however, is sometimes restricted because of economical or technical constraints.[2, 3] On the other side, there is a growing concern to establish a sustainable society that maintains systems of recovery and recycling of valuable metals taking account of the shortage of mineral resources in future as well as the removal of toxic metals from the environment. To date, the majority of the heavy metals in wastewater are removed by means of precipitation by adding calcium hydroxide, in which large amount of non toxic metal compounds such as calcium sulphate are also precipitated together with heavy metals as precipitated sludge, which are dumped in the landfill sites. It is not only difficult to meet stringent environmental regulation by means of precipitation technique, but also unavailability of landfill sites. On the other hand many heavy metals contained in these are valuable and indispensable resources. Therefore for a sustainable society in future, it is necessary to recover metal resources from various wastes instead of discarding the landfill sites. Although, adsorptive recovery and removal using ion exchange chelating resin could be an alternative, however such an approach is expensive taking account of the post treatment of spent resin and in addition, it also poses other environmental problems if such synthetic plastic materials are incinerated.[5]

Recently, biosorption has emerged as an alternative treatment technology for heavy metals removal. Biosorption is more economical and provides a greater metal removal capacity, overall at very low metal concentration where traditional technologies become expensive and ineffective.[4] The two most important advantage of using biosorbent are; they are cheap and are available in the form of waste. There are different biological substrates tested in biosorption with either modified or unmodified form such as fly ash, peanut hulls, almond hulls, cotton seed hulls, maize barn, different algae, crab shells, rice husk, sugarcane bagasses etc.[6]

Biosorption is the ability to accumulate the heavy metals from aqueous solution by certain types of microbial biomass.[7] Biosorption of metals is not based on only one mechanism. It consists of several ones that quantitatively differ according to the type of biomass. Metal sequestration may involve complex mechanisms mainly; ion exchange, chelation, adsorption by physical forces and ion entrapment in inter and intra fibrilar capillaries and spaces of the structural polysaccharides cell wall net work. [8]

In the context of Nepal, peoples are extremely unaware of the heavy metal pollution. This may be due to the illiteracy and lack of government policy. The hospital wastes, industrial wastes as well as other household wastes that may include noxious heavy metals are directly disposed into the river. Similarly peoples are extensively using different insecticides, fungicides, pesticides and agricultural fertilizers which may contain the heavy metals and are the major source of the ground water contaminant. In addition to this, in the Terai region of Nepal, tubewel water has the upper level of the Arsenic and is the burning problem. So there is the growing concern for the development of suitable biosorbent. In Nepal, apple is the most abundant fruit found in almost at all seasons. Apple plants are especially found in mountains and hilly region of Nepal like Manang, Mustang, Humla, Jumla, Helambu etc. The apple wastes are released abundantly from the wine factories, juice vending centers as well as a household waste after juicing. Xanthated apple waste is one of the effective chemically modified biosorbent for the adsorption of most of the heavy metals as well as the anionic species such as arsenic, phosphate, nitrate after the material is loaded with iron.

In the present study, apple waste was modified into an effective adsorbent by the xanthation process. The xanthation reaction is carried out by the reaction between dry apple waste and carbon disulphide under the alkaline condition. But the optimum concentration of the alkali for the xanthation process has not been studied yet. Hence, in the present study, the optimization of the concentration of NaOH for the xanthation of apple waste was done. For this, the apple waste was xanthated at 5%, 10%, 15% and 20% NaOH concentration in dry condition. From the adsorption behavior of Iron and by the evaluation of total exchangeable protons from four types of XAW, the optimization of NaOH was done. Then, the adsorption behavior of Aluminium metal was studied only onto the optimized XAW.

1.2. Adsorption Study

The term adsorption is used to describe the fact that there is a greater concentration of the adsorbed molecules at the surface of the solid than in the gas phase or in the bulk solution. The adsorption study is mainly conducted by the following two methods.[9]

1.2.1 Packed Column Experiment

In this experiment, a glass column of particular length and internal diameter is filled with known amount of the adsorbent. With the help of the porous sheet at the bottom of the column, the adsorbent bed is supported inside. This also provides the uniform inlet flow and good liquid distribution. The top of the bed is generally closed by a layer of glass bead (1 mm diameter) which avoids the loss of biomass and also ensures a closely packed arrangement.[4] A known concentration of the metal solution is fed through the bed in up flow mode at the desired flow rate with a peristaltic pump connected at the bottom of the column. Samples are collected periodically and filtered through cellulose nitrate filter paper. The filtrate is then analyzed for the remaining metal ion concentration. Operation of the column is stopped when the effluent metal concentration reached a constant value. [4]

1.2.2. Batch Adsorption Experiment

In the batch adsorption study, a definite volume of the metal solution having known concentration is taken in a 125 mL stoppered bottle. A definite mass of the adsorbent is added to it and the stoppered bottle is vigorously shaken in a mechanical shaker at room temperature for 24 h to ensure the adsorption equilibrium. The initial and final concentrations of metal ions are determined by using either AAS or spectrophotometer. Heavy metal adsorption onto different adsorbent is affected by different parameter such as initial concentration of metal ions (mg/L), contact time (sec), amount of the adsorbent used (g/L), temperature and pH of the solution.[8] To understand the mechanism and effectiveness of adsorption, one of the above parameter is changed by keeping other constant. From the measurement of the metal concentration before and after the adsorption, weight of the dry adsorption gel and from the volume of aqueous solution, the amount of adsorbed metal is calculated using following equation.[10]

$$q_t = \frac{(C_i - C_e)V}{W} \qquad \text{(I)}$$

Where, C_i and C_e are the metal ion concentration in mg/L initially and at equilibrium, respectively. V is the metal solution in liter and W is the weight of adsorbent in gram.

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 (II).

$$D = q_e/C_e \qquad \text{(II)}$$

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).

Percentage adsorption of metal is defined as the ratio of the decrease in metal ion concentration after adsorption to the initial concentration of metal ions in aqueous solution. Percentage adsorption is determined by the following expression.

$$A(\%) = \frac{(C_i - C_t)100}{C_i} \qquad \text{(III)}$$

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

1.3. Adsorption Isotherm

To describe the distribution of the solute in the solid phase and the liquid phase at equilibrium conditions, it is necessary to express the amount solute adsorbed per unit weight of the adsorbent, q, as a function of the residual equilibrium concentration, C_o, of solute remaining in solution. The expression of this relationship is termed as adsorption isotherm.[11] With the help of experimental isotherms, one can describe the adsorption capacity to evaluate the feasibility of this process for a given application.[12] There are different types of adsorption isotherm equations namely Langmuir, Freundlich, Temkin and Duinin-kaganer-Radushkevich (DKR) isotherms equations. But Langmuir and Freundlich adsorption isotherms equations are most widely used to represent the data of sorption from aqueous solution.

Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is the best known of all isotherms describing adsorption and it has been successfully applied to many adsorption processes. Langmuir isotherm is used to describe single layer adsorption. The isotherm can be represented by following expression.[6]

$$q_e = \frac{q_m b C_e}{1+bC_e} \qquad \text{(IV)}$$

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 experimental data and its parameter evaluation, the rearranged and linear form of Langmuir isotherm equation is given as,

$$\frac{C_e}{q_e} = 1/bq_m + Ce/q_m \qquad (V)$$

From the experimental C_e and q_e data, the linear plot of C_e/q_e against C_e can be applied to evaluate the Langmuir constants: q_m and b, from the slope and intercept, respectively for all metals. The values obtained from the Langmuir model (q_m and b) can provide information in the screening of the sorbent. The more favorable sorbent is indicated by the higher value of the slope of an adsorption isotherm. It means that potentially a good sorbent can be comparatively evaluated from values of q_{max} and b. However, the Langmuir gives no the mechanistic aspects of sorption. [13]

Freundlich Adsorption Isotherm

It is an empirical model that is based on adsorption on heterogeneous surface. Linearised form of Freundlich equation is given by the relation.

$$q_e = KC_e^{1/n} \qquad (VI)$$

This equation may also be written in the logarithmic form as

$$\log q_e = \log K + 1/n \log C_e \qquad (VII)$$

Where, C_e is the equilibrium concentration (mg/L) and q is the amounts of metal adsorbed at equilibrium (mg/g). K is the constant and is the indicator of the adsorption capacity depending upon the nature of both adsorbent and adsorbate. While n is the constant dependent upon the nature of the adsorbate. The value of 1/n varies between 0.1 and 1.0 indicates the favorable adsorption.[14]

1.4. Study of Adsorption Kinetics

Adsorption kinetics deals with the study of the rate and mechanism of the adsorption phenomenon. It is well recognized that the characteristics of sorbent surface is a critical factor that affects the sorption rate parameters and that diffusion resistance plays an important role in the over all transport of the solute. There are mainly three kinetic models to describe the adsorption phenomena. The relationship between experimental data and the model predicted value is expressed by correlation coefficient.[3]

The Pseudo First-Order Model

The pseudo first order kinetic model is applicable for the reversible reaction with an equilibrium being established between liquid and solid phase. To evaluate the differences in biosorption kinetic rate and metal recoveries, the kinetics of metal adsorption is described with pseudo first order model. The pseudo-first order rate equation (Lagergren, 1898) to study the kinetics of heavy metal adsorption is given by,

$$dq_t/d_t = k_1(q_e-q_t) \qquad \text{(VIII)}$$

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 (min^{-1}).

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

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

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

Most of the sorption systems followed a pseudo second order kinetic model as reported by Ho and Mckay(1999). It is based on the sorption capacity on the solid phase. The pseudo second-order reaction rate equation (Ho and 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;

$$dq/dt = k_2(q_e-q_t) \qquad (X)$$

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 $q_t = q_t$ at $t = t$, gives rearranged linear form as,

$$t/q_t = 1/k_2q_e^2 + 1/q_e\, t \qquad (XI)$$

If the initial adsorption rate is υ_o (mg/g.min), then $\upsilon_0 = k_2\, q_e^2$.

The equation (XI); can be written as,

$$t/q_t = 1/\upsilon_o + 1/q_e\, t \qquad (XII)$$

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,

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

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 $q_t = q_t$ at $t = t$, the linear form of equation (XIII); becomes,

$$1/ q_e\text{-}q_t = 1/q_e - k'_2 t \qquad \text{(XIV)}$$

The plot of $1/q_e\text{-}q_t$ 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 investigated 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).

Opposing to other well established model, pseudo second-order model predicts the behavior over the whole range of studies and it is in agreement with a chemisorptions mechanism being the rate controlling step with the formation of monolayer coverage on the adsorbent surface (McKay *et al.*, 1999).[12]

1.5. Mechanism of Adsorption

The adsorption can be explained by an ion exchange mechanism. The natural apple waste constitutes mainly 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 up taking 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. Since the adsorption behavior of XAW 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 through the formation of stable ring chelates as shown in below scheme.

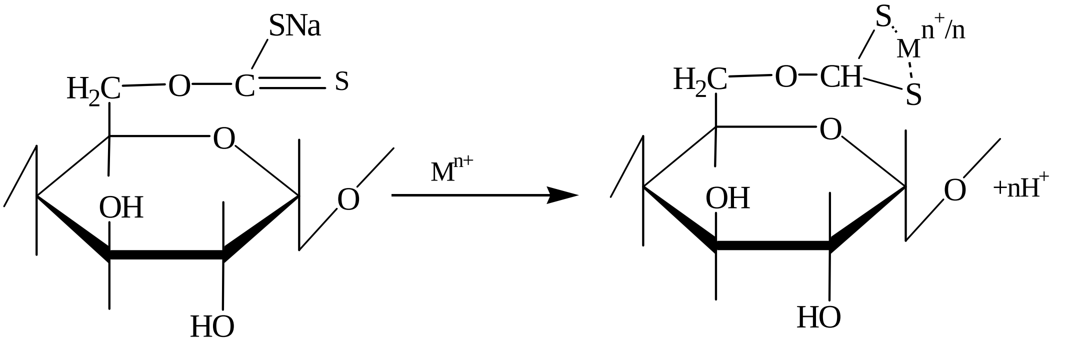

Fig: 1. Adsorption Mechanism for Ionic Species onto Monomeric Unit of Xanthated Apple Waste.

1.6. Spectrophtometric Determination of Iron

Numerous reagents have been reported for the determination of iron; for e.g. Thiocyanate, dipyridine, tripyridine and 1, 10-phenonthroline etc. The spectrophotometric determination method of a red orange complex that forms between iron(II) and 1,10- phenonhroline is practical and sensitive.[15,16] The molar extinction coefficient of ferrous iron complex with 1,10-phenonthroline complex is 11000. The orange red phenonthroline complex $(C_{12}H_8N_2)_3$ Fe^{++} can be formed quantitatively in the pH range 2-9 with the suitable reagent concentration.[17, 19]

Ferric iron can be reduced with hydroxylamine hydrochloride. The pH can be adjusted at 4.5 using the acetate buffer. Aside from colored ions, the following ions interfere to a greater or less extent. Silver and bismuth give precipitates. Certain divalent metals such as cadmium, mercury and zinc form slightly soluble complexes with the reagent and reduce the intensity of the iron color, but interference can be reduced by adding a larger excess of the reagent. A great advantage of 1, 10-phenonthroline over some other iron reagents lies in the possibility of using it in slightly acidic solution.[16, 20]

1.7. Spectrophotometric Determination of Aluminium

There are several reagents for the spectrophotometric determination of aluminium ion but Eriochrome cyanine R is more superior to others. With this reagent, dilute aluminium solutions buffered to a pH of 6.0 produce a red to pink color complex that exhibits maximum absorption at near about 535 nm. [15] The intensity of the developed color is influenced by the aluminium concentration, reaction time, temperature, pH, alkalinity and concentration of the other ions in the sample. The minimum and maximum concentration range detectable by this method in the absence of fluorides and complex phosphate is approximately 6 ppb-400 ppb. A pure reagent should be brick red in color which fades to a pale yellow color in about two weeks. [16] It appears that the form of the dye which reacts with aluminium ion is the strongly colored one. Hence, it is most important for the optimization of the reagent that should be added in complex formation.

1.8. Introduction and Harmful Effects of Aluminium

Aluminium is the second element of group IIIA of the periodic table, has an atomic number of 13 and atomic weight of 26.98.[27] The average abundance in the earths crust is 8.1%, in soil it is 0.9 to 6.5%, in streams it is 400 µg/L and in ground water it is less than 0.1 µ/L.[15] Aluminium occurs in the earth crust in combination with silicon and oxygen to form feldspars, micas and clay minerals. Aluminium and its alloys are used for heat exchangers, aircraft parts, building materials, containers etc. In our country, it is used in almost of all utensils.

Aluminium is non essential for plants and animals. The United Nations Food and Agricultural organization recommended maximum level for Irrigation is 5 mg/L. In the state of excess total aluminium, the most effected tissues are bone, lung, spleen, liver and brain. Aluminium has been implicated as a cause of Azlimers disease which is chronic progressive disease clinically characterized by gradual loss of cognitive function. Other toxic effect of aluminium includes anemia, dentalcaries, kidney and liver dysfunction, neuromuscular disorders, osteomalacia and blood disorders.[15]

1.9. Introduction and Harmful Effects of Iron

Iron is the first element in group VIII of the periodic table. It has atomic number 26, and atomic weight 55.85 and common valencies of 2 and 3. It averages about 0.7 mg/L in streams and 0.1 to 10 mg/L in ground water.[27] Because ground water is often anoxic, any soluble iron in ground water is usually in the ferrous state. On exposure to air or addition of oxidant, ferrous iron is oxidized to the ferric state and may hydrolyze to form red, insoluble hydrated ferric oxide.[28] Elevated iron levels in water can cause stains in plumbing, laundry and cooking utensils and can impart objectionable tasks and color to the foods. The United Nations Food and agriculture Organization recommended level for irrigation waters is 5 mg/L. The US EPA secondary drinking water standard MCL is 0.3 mg/L. High iron content in water can cause disease known as siderosis which is found in some African tribes who use iron pots to prepare a special type of beer.[15]

2. Literature Review

Water pollution due to toxic heavy metals remains a serious environmental and public problem. Therefore, numerous approaches have been studied for the development of cheaper and effective metal sorbents such as fly ash, peat, microbial bio mass and agricultural by-product.

Adsorption was first observed by Lowitz in 1785 and soon applied as a process of removal of color from sugar during refining.[21] In 1929, the first granular activated carbon (GAC) units were constructed for the treatment of water supplies in Hamm, Germany, and in 1930 at Bay City. Then, adsorption on activated carbon become the recognized method for the removal of heavy metals from waste water while the high cost of activated carbon limits its use in heavy metal adsorption.[21] Hence, a search for the low cost and easily available adsorbent had led to the investigation of materials of agricultural and biological origin as potential metal sorbents.

In the literature search for the chemical modification of the bioadsorbent, Ghimire *et. al.* [22] modified the orange waste by the saponification process. The total exchangeable cation of the saponified orange waste was found to be 2.64 mol/kg. They used the adsorbent for the removal of phosphate after the iron(III) is loaded on it. Ghimire *et. al.* [10] also chemically modified the orange waste by phosphorylation reaction. The maximum iron loading capacity for the gel was found to be 3.7 mol/kg. They used the iron loaded gel for the removal of arsenic.

Upendra Kumar and Manas [14] chemically modified the rice husk by treating the raw rice husk by treating it with the epichlohydrin, NaOH and Na_2CO_3 separately. The researchers used the modified rice husks for the removal of Cadmium. They found that the maximum adsorption capacities were found to be 8.58, 11.12, 20.24 and 16.18 mg/g, respectively for raw rice husk, epichlorated rice husk, NaOH treated rice husk and Na_2CO_3 treated rice husk.

Parajuli *et. al.* [23] prepared the crosslinked lignocatechol gel by immobilizing catechol onto wood lignin, followed by cross linking. They used this adsorbent for the removal of different heavy metals.

Hawari *et. al.* [7] prepared the H-biomass by combining untreated biomass with 0.02M HCl for 3 h at a biomass concentration 20 g/L and pH value close to 2.5. They also prepared the Ca-biomass and K-biomass by treating the raw biomass with 0.01M $Ca(OH)_2$ and 0.02M KOH, respectively.

Ghimire *et. al.*[5] modified the sea weed *Laminaria japonica* by cross linking with epichlorohydrin. They studied the adsorption behavior of trivalent and divalent metal ions on it. It was found that it exhibits excellent selectivity towards certain heavy metals. The researcher [24] also modified the sea weed *Porphyra yezoensis* and *Ulva japonica* by cross linking with calcium. They found that the maximum adsorbent capacity for the removal of Pb(II) was 0.67 mol/kg dry gel.

On the literature view of chemical modification of the bio adsorbent by Xanthation reaction, Nalini Sankararamakrishna, Rashmi Sangh[25,26] prepared and characterized the novel xanthated chitosan. They first prepared the chitosan from the partial deacetylation of chitin in alkaline medium. Then, they used Glutaraldehyde for cross linking the chitosan beds and obtained cross linked chitosan beads. They used 14% NaOH for the xanthation of cross linked chitosan beads. They used xanthated chitosan for the removal of hexavalent chromium.

3. Objectives of the Study

Biosorption is the most convenient and effective technique for the heavy metal removal from the waste water. In the present study, the optimum alkaline condition for the xanthation of apple waste and its adsorption behavior for iron(III) and aluminium(III) were investigated. The main objectives of the present study can be summarized as follows.

1. To prepare the novel adsorbent from the xanthation of apple waste.
2. To optimize the alkaline condition of the solution for the xanthation of apple waste.
3. To evaluate the total exchangeable hydrogen ions in all four types of xanthated apple waste xanthated at 5%, 10%, 15%, and 20% NaOH concentration.
4. To determine the iron loading capacity of xanthated apple waste which are xanthated at 5%, 10%, 15%, and 20% NaOH concentration.
5. To investigate the adsorption behavior for Fe(III) and Al(III) towards the xanthated apple waste from aqueous solution.
6. To find the adsorption isotherm of Fe(III) and Al(III) on xanthated apple waste.
7. To find out the equilibrium time for the adsorption of Fe(III) and Al(III) on xanthated apple waste.
8. To study the kinetics behavior of adsorption of Fe(III) and Al(III) on xanthated apple waste.

4. Experimental Section

4.1. Preparation of Reagents

4.1.1. 0.1 N Nitric Acid (Approx.)

0.1N nitric acid solution was prepared by mixing 6.25 mL of conc. nitric acid in 1000 mL of volumetric flask in distilled water.

4.1.2. 2M NaOH Solution (Approx.)

20 gm of NaOH pellets was dissolved in 250 mL volumetric flask and volume was made up to the mark.

4.1.3. 5% NaOH Solution (Approx.)

12.5 gm of NaOH pellets was dissolved in 250 mL volumetric flask and volume was made up to the mark.

4.1.4. 10% NaOH Solution (Approx.)

25 gm of NaOH was dissolved in 250 mL volumetric flask in distilled water and volume was made up to the mark.

4.1.5. 15% NaOH Solution (Approx.)

37.5 gm of NaOH was dissolved in 250 mL volumetric flask in distilled water and volume was made up to the mark.

4.1.6. 20% NaOH Solution (Approx.)

50 gm of NaOH was dissolved in 250 mL volumetric flask in distilled water and volume was made up to the mark.

4.1.7. Ferric Chloride Stock Solution

Stock solution of iron(III) was prepared by dissolving 4.84 gm of a hexahydrate Ferric chloride [$FeCl_3.6H_2O$] of Merck in 1000 mL volumetric flask using 0.1M nitric acid with volume up to the mark.

1 mL of $FeCl_3$ stock solution= 1000 µg of Fe (III)

4.1.8. Iron(II) Stock Solution

An iron(II) stock solution was prepared by dissolving 7.016 gm of Mohr’s salt [$Fe(NH_4)_2.FeSO_4.7H_2O$] (S.D. Fine-Chem. Limited) in 1000 mL volumetric flask in distilled water with volume up to the mark.

1 mL of stock solution= 1000 µg of Fe(II)

4.1.9. Preparation of Aluminium(III) Stock Solution

35.167 gm of Potash alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$) (B.D.H. Chemicals Limited) was dissolved in 1000 mL volumetric flask with 0.1M Nitric acid and volume was made up to the mark.

1 mL of the stock solution=1000 µg of Al(III)

4.1.10. 0.1 M Acetic Acid

1.43 mL of glacial acetic acid (Qualigens Fine Chemicals) was taken in 250 mL volumetric flask and the volume was made up to the mark.

4.1.11. 0.1M Sodium Acetate Solution

2.05 gm of anhydrous sodium acetate [CH_3COONa] (Labort Fine Chemicals PVT Limited) was taken in 250 mL volumetric flask. It was dissolved in distilled water and volume was made up to the mark.

4.1.12. 0.20% 1, 10-Phenonthroline Monohydrate Solution

0.20 gm of 1, 10-phenonthroline monohydrate was taken in a 100 mL volumetric flask. It was dissolved in distilled water by heating up to temperature 60°C but not allowed to boil. After complete dissolving, the volume made up to the mark and flask was covered by black paper for the prevention of transmission of light.

4.1.13. pH 4.5 Buffer Solution

6.5 mL of 0.1M acetic acid solution and 0.1M sodium acetate solution was mixed homogenously in 100 mL volumetric flask.

4.1.14. 10% Hydroxyl Amine Hydrochloride Solution

10 gm of solid hydroxyl amine hydrochloride (S.D. Fine-Chem. Limited) was placed in 100 mL volumetric flask. It was dissolved in distilled water and volume was made up to the mark.

4.1.15. 0.2% of Eriochrome Cyanine R Solution

200 mg of Eriochrome cyanine R was dissolved in distilled water in 100 mL volumetric flask. The volume was then made up to the mark.

4.1.16. pH 6 Buffer Solution

38 gm of anhydrous sodium acetate was dissolved in distilled in 1000 mL volumetric flask. 2.30 mL of glacial acetic acid was added on it. The volume was then made up to the mark

4.1.17. Standard Buffers of pH 4, pH 7 and pH 9.2

Buffer solutions of pH 4, pH 7 and pH 9 were prepared by dissolving buffer tablets of pH 4, pH 7 and pH 9 in 100 mL volumetric flasks in distilled water.

4.1.18. Working Solution of Metals

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

4.2. Preparation of Adsorbent

4.2.1. Preparation of Raw Adsorbent from Apple Waste

The crude apple waste was purchased from local juice center located at Bhotahiti, Kathmandu. The apple waste was dried in sun light for about a week. It was further dried in electric hot air oven at 60 ^{o}C for 24 h. The dried apple waste was then powdered in grain crusher. The powdered raw adsorbent was packed in air tight bottle.

4.2.2. Chemical Modification of Raw Apple Waste

The adsorbing capacity of the raw apple waste was largely enhanced by its chemical modification i.e. Xanthation reaction. 10 gm of powder raw adsorbent was taken in two necks round bottom flask. 100 mL of 5% NaOH was added slowly to it with constant shaking. 10 mL carbon disulphide was added. The flask was made air tight and shaken for 24 h in a mechanical shaker.

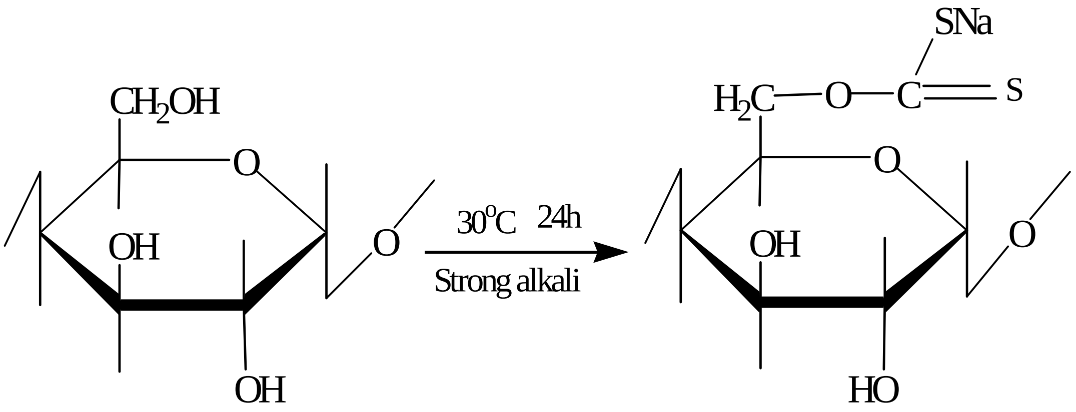

Fig: 2. Plausible Mechanism for the Xanthation process onto Monomeric Unit of Cellulose Contained in Apple Waste.

The material was then washed with distilled water till neutrality. The material was filtered and was dried in sun light for about 3 days. Finally, the material was dried in hot air oven for 24 h at 60 ^{o}C. The material was then pulverized in the form of fine powder in mortar.

It was passed through sieve to get uniform size adsorbent. The adsorbent was then called xanthated apple waste (XAW). The same procedure was repeated again but with NaOH concentration 10%, 15% and 20% respectively. Hence, finally we had four types of xanthated apple waste xanthated at 5%, 10%, 15% and 20%, respectively.

4.2.3. Characterization of Adsorbent by Evaluating Total Exchangeable Protons

One gm of each of the four types of xanthated apple waste was separately shaken with 50 mL of 0.1N hydrochloric acid for 24 hour in a mechanical shaker. They were washed with distilled water till neutrality. Then, they were filtered in a filter paper. The residue were first dried in sun light and then in hot air oven at 60 °C. The H^+ form of the XAW were used to evaluate the total exchangeable protons.

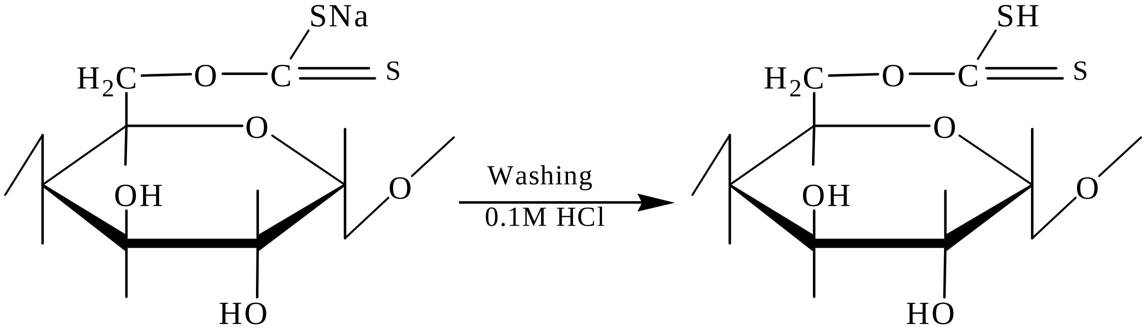

Fig: 3. **Preparation of H^+- form Gel by Washing with Dilute Hydrochloric Acid Solution**

50 mL of 0.1M NaOH was taken in 125mL stoppered bottles and 50 mg of H^+ form of XAW was added to it. The bottles were then shaken for 24 h in a mechanical shaker. This was then filtered and filtrate was titrated with 0.1N oxalic acid. The decrease in sodium hydroxide concentration must be equal to the total amount of H^+ (exchangeable) that is released from the adsorbent. From these, total exchangeable protons were evaluated in each of four types of XAW. Blank systems with 50 mL deionised water (no base added) and 50 mg H^+- gel (each of four types separately) were also shaken simultaneously to determine any residual influence of acid onto the XAW-gels.

4.3. Construction of Calibration Curve for Iron

1 ppm, 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 8 ppm and 9 ppm iron(II) solution along with the required reagents *i.e.* 5 mL buffer solution of pH 4.5, 3 mL of 10% hydroxyl amine hydrochloride solution and 2.5 mL 20% 1,10-phenonthroline solution were prepared in nine 25 mL volumetric flask. A blank solution was prepared by adding all the reagents but with no iron solution. The solutions were allowed to leave for 30 minutes to develop the full color. An intermediate concentration of iron solution was taken for

the determination of λ_{max}. For this, the spectrophotometer was set to zero by using blank solution. Then, the absorption of light by the intermediate concentration of the solution at different wavelength was measured. The spectrophotometer was set to zero every times of changing wavelength with the help of blank solution. At last, a plot of absorption of light v_s corresponding wavelength was plotted. From the graph, the value of λ_{max} was evaluated.

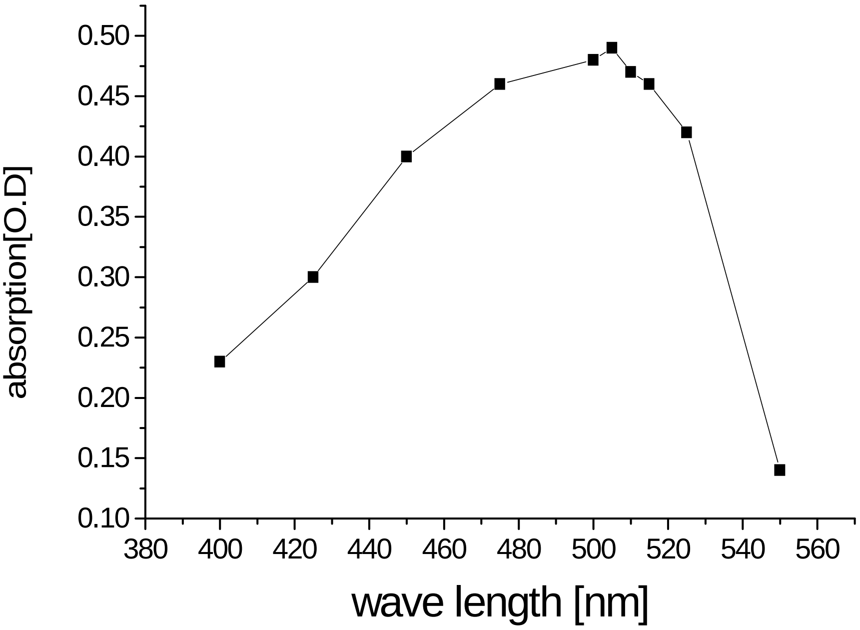

Fig.4. Absorption Spectrum of Iron(II) Complex with 1,10-phenonthroline

After finding the λ_{max}, the spectrophotometer was fixed at that wavelength and the absorption of light by each solution was measured. The calibration curve for the iron was obtained by plotting the absorption of light vs. corresponding concentration of the metal solution.

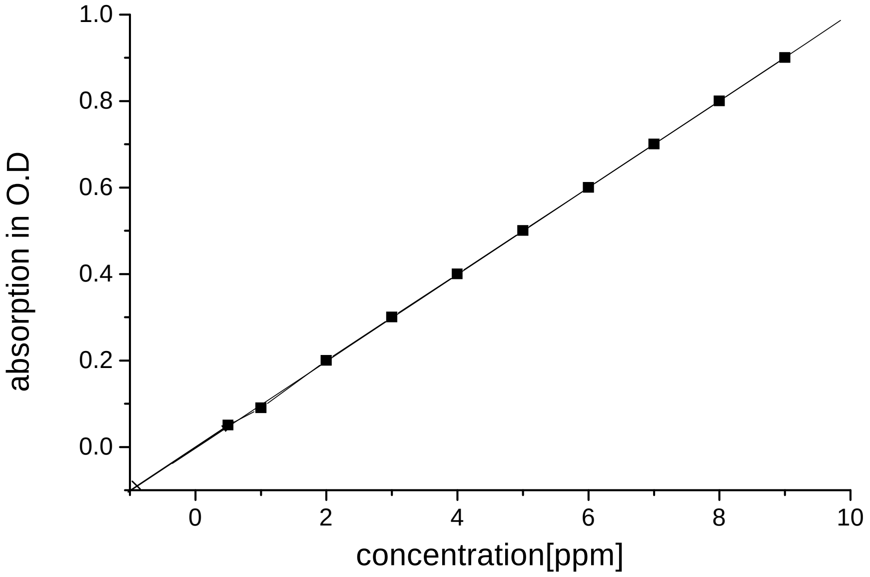

Fig.5. Calibration Curve for Iron

4.4. Construction of Calibration Curve for Aluminium

Nine, different 25 mL volumetric flask were taken. In them, 0.5 mL, 1 mL, 2 mL, 3 mL, 4 mL, 5 mL, 6 mL, 7 mL and 8 mL of 1.25 ppm aluminium(III) solution were placed. Then, 5 mL of buffer of pH 6.0, 1 mL of Eriochrome cyanine R (0.20%) were added in all of them. The volume in each flask was made up to the mark. The concentration of the aluminium solution in nine volumetric flasks become 25 ppb, 50 ppb, 75 ppb, 100 ppb, 150 ppb, 200 ppb, 250 ppb, 250 ppb, 300 ppb, and 400 ppb, respectively. A blank solution was prepared by using same amount of all the reagents but with no aluminium(III) solution. The solutions were allowed to leave for 15 minutes for full color to be developed.

After 15 minutes, a solution of the intermediate color was taken and its absorption of light was measured at different wavelength. At every wavelength, the spectrophotometer was set to zero with the help of blank solution. Then, a plot of absorption vs. wavelength of light was plotted. From this plot the λ_{max} was evaluated which was 525 nm.

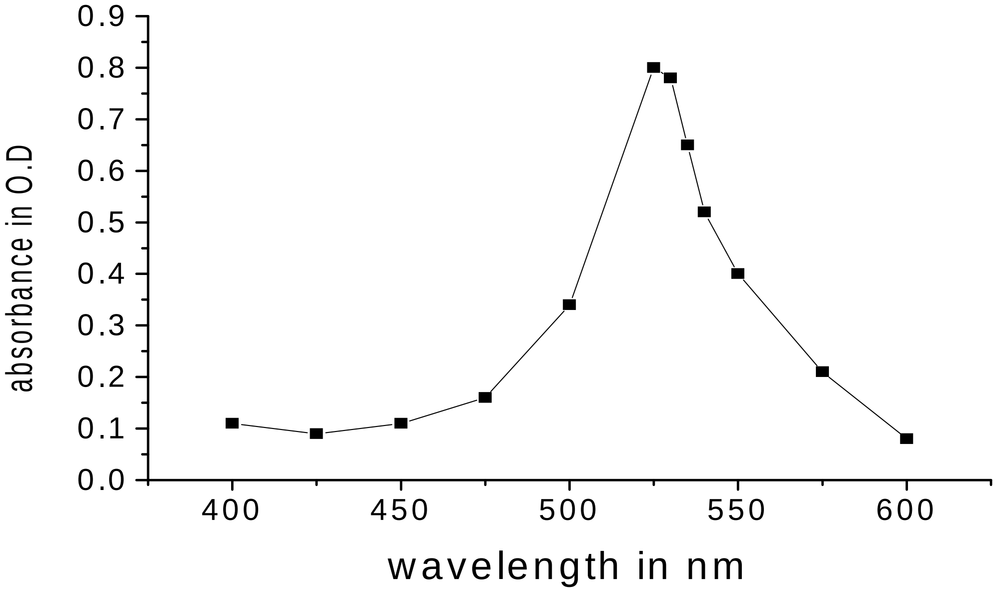

Fig.6. Absorption Spectrum of Al(III) Complex with Eriochrome Cyanine R

The absorption of light by each of the solution was measured by fixing the spectrophotometer at wavelength 525 nm. Before the measurement, the spectrophotometer was set to zero by using blank solution. At last, a plot of concentration vs absorption or light was made which is the calibration curve for the aluminium

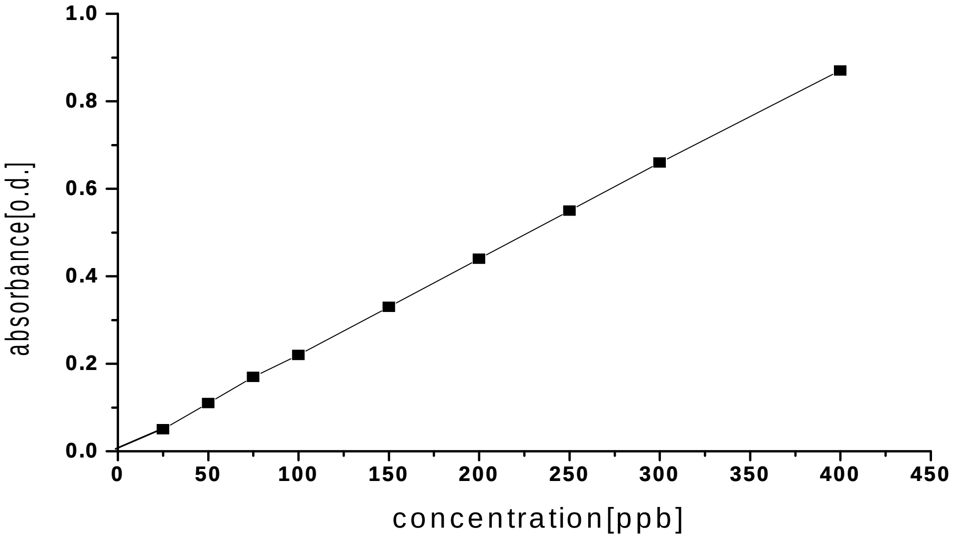

Fig.7.Calibration Curve for Al(III)

4.5. Batch Adsorption Studies

Batch adsorption studies were carried out to determine the adsorption behavior of Fe(III) onto four types of XAW, xanthated at 5%, 10%, 15%, 20% NaOH concentration. From this, the effect of initial pH, effect of initial concentration of metals, and effect of contact time was investigated. From the adsorption isotherm of iron on four types of XAW, the optimization of NaOH on the Xanthation of apple waste was investigated. Then the batch adsorption studies for aluminium were carried out only with the optimized XAW to investigate the adsorption behavior and adsorption isotherm. The pH of the metal solutions were adjusted at the required pH by using 2N HNO_3 and 2N NaOH solution. For the batch adsorption 20 mL of the metal solutions were taken in 125 mL stoppered bottles and 20 mg of the adsorbent were added to each of them. The bottles were shaken in a mechanical shaker for 24 at room temperature. Then the solutions were filtered using filter paper and filtrates were analyzed for the determination of equilibrium concentration. Concentration before and after the adsorption were determined by ‘Systronics

103’ spectrocolorimeter. Before the analysis, the filtrates were diluted to certain concentration such that they were in the measurable range of the spectrophotometer.

4.5.1. Batch pH Studies

Batch pH studies were carried out for the determination of optimum pH for adsorption. This was performed for iron by shaking 20 mL of metal solution having concentration 20 mg/L with 20mg of adsorbent. The initial pH taken were 1.0, 1.5, 2.0, 2.5, and 3.0. Similarly for the aluminium, 20 mL of the solutions with concentration 10 mg/L were shaken with 20 mg of optimized XAW at pH 2.0, 3.0, 4.0 and 5.0, respectively.

After shaking for 24 h in mechanical shaker each solution were filtered in the filter paper and equilibrium pH of the filtrate was noted. The filtrates were then analyzed for the equilibrium concentration. From, the value of equilibrium concentration and initial concentration, the percentage adsorption at each pH were calculated by which optimum pH of the adsorption was evaluated.

4.5.2. Batch Isotherm Studies and Optimization of XAW

For the batch isotherm studies, the initial concentrations of the metal solutions taken were ranged from 25 mg/L to 500 mg/L for both iron and aluminium. The initial pH of the solutions was maintained at their respective optimum pH values before the adsorption. Here, also for each concentration, the volumes of the solution taken were 20 mL and weight of the adsorbent was 20 mg. The solutions were shaken in a mechanical shaker and metal concentration before and after the adsorption were analyzed by using spectrophotometer.

The data obtained were then analyzed for Langmuir and Freundlich isotherm. The isotherm study was performed on all four types of XAW. On the basis of the adsorption isotherm the optimization of XAW was done. Then the isotherm study for aluminium was performed only with the optimized XAW.

4.5.3. Batch Experiment for the Optimization of Time

After determining the optimum pH, the equilibrium time for the adsorption of iron(III) and Al(III) were studied at their respective optimum pH values at room temperature. For the experiment, 20 mL of the solutions were shaken with 20 mg of the adsorbent. The initial concentrations of the metal solution were 50 mg/L and 20 mg/L for iron and aluminium, respectively. The solutions were shaken for 5 min, 10 min, 15 min, 30 min, 45 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h, 9 h, 10 h and for infinite time, respectively. The solutions were filtered in a filter paper at exactly predetermined duration of time. The filtrates were then analyzed for the final concentration of the metal solution with the help of spectrophotometer. The optimization of time was done only with the optimized XAW.

4.5.4. Batch Kinetic Studies

Batch kinetic studies for the aluminium and iron were performed only with optimized XAW. The experiments were carried out by shaking 20 mL of the solution with 20 mg of the adsorbent. The concentration of the iron solution for this was 50 mg/L and aluminium solution was 20 mg/L. The bottles were shaken for the times ranging from 5 min to 90 min. The data obtained were then analyzed for pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and Mckay *et.al*, 2000) and second order (Lagergren, 1898) kinetics model.

5. Results and Discussion

5.1. Determination of Total Exchangeable Proton

The total exchangeable protons were found to be 3 mole/kg, 4 mole/kg, 6 mole/kg and 6 mole/kg in four types of XAW xanthated at 5%, 10%, 15%, and 20% NaOH concentration, respectively.

The above result showed that the extent of xanthation in apple waste increases with the increase in alkaline condition from 5% NaOH concentration to 15% NaOH concentration. However, further increase in NaOH concentration had no effect on the total amount of exchangeable protons. Hence, the optimized condition of NaOH for the xanthation of apple waste was found to be 15% which is also shown in Fig. 20.

5.2. Batch pH Study

It is well known that pH of the aqueous solution is an important parameter in the adsorption and ion exchange process and hence in metal removal by adsorption. According to the Fig.1, the percentage adsorption of iron increased from 0% to 59.4%, 2.5% to 77.4%, 2.38% to 88% and 7.5% to 78.3% for four types of XAW xanthated at 5%, 10%, 15%, and 20% NaOH concentration, respectively when the pH is increased from 1.0 to 3.0. The initial concentration of the iron(III) solution taken for pH maintenance was 20 mg/L. But when the concentration of the solution was measured just after the pH was maintained; the initial concentration of the solution of pH 3 extremely falls to around 10 mg/L. This indicates the hydrolysis of Fe(III) at that pH. From the analysis of the data and graph (Fig.8), the optimum condition for the iron adsorption was found to be at pH 2.5.

Similarly, the data and graph (Fig.9) of the batch pH study of the aluminium(III) shows that the percentage adsorption increases from 10% to 75% when the pH had increased from 2 to 5. Since, the sample maintained at pH 5 had shown hydrolysis phenomena, a pH 4 was chosen as the optimum pH for adsorption of aluminium(III) for further analysis.

The increase in percentage adsorption with the increase of pH indicates that the adsorption process involves the cation exchange mechanism. At the low pH value, there is higher concentration of the protons than the concentration of metal ions and protons tend to attach with the adsorbent molecule. But at the high pH, the concentration H^+ ion is less and they are easily replaced by the metal ions onto the adsorbent by the ion exchange process.

5.3. Optimization of Time Studies

According to the Fig.16, the optimized time for the adsorption of iron(III) and aluminium(III) was found to be 3 h and 8 h, respectively. The data table shows that the initial rate of adsorption is high. This is because initially there are large numbers of cation exchange sites. The rate of adsorption decreases with time due to the decrease in the active sites in the adsorbent. When all the active sites are occupied by the metal ions, equilibrium is attained and the rate of adsorption becomes zero.

5.4. Batch Kinetic Studies

The data obtained from the kinetic experiment for the adsorption of Fe(III) and Al(III) were analyzed using pseudo-first order, pseudo-second order, and second order kinetics models. The respective plots for pseudo-first order, pseudo-second order and for the second order kinetic models are shown in the Fig.17, 18 and 19. The plot for pseudo-second order model gave perfect straight lines for both metals, Fe(III) and Al(III). Hence, we can say that the adsorption of Fe(III) and Al(III) on XAW gel took place by pseudo-second order mechanism. This is further confirmed by the highest value of correlation coefficient for the pseudo-second order plot. The different parameters for the three kinetics plots are shown in following table.

Table: 1. Kinetic parameter for the metal biosorption with correlation coefficient

Metal	q_{exp} mg/g	Pseudo first-order			Pseudo second-order				Second-order		
		k_1 x 10^{-3} (1/min)	q_e mg/g	R^2	k_2 x 10^{-3} g/mg.min	q_e mg/g	R^2	υ_o mg/g.min	k_2'x 10-3 g/m.	q_e mg/g	R^2
Fe(III)	47.00	25.50	17.80	0.97	3.99	47.80	0.99	9.12	6.40	13.40	0.59
Al(III)	16.75	4.40	4.21	0.89	8.00	15.24	0.99	1.86	1.90	4.50	0.98

The values of predicted equilibrium sorption found to be in 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.

5.5. Batch Isotherm Studies

The Langmuir isotherm and Freundlich isotherm for the adsorption of Fe(III) on four types of XAW xanthated at 5%, 10%, 15% and 20% NaOH concentration is shown in the Fig.12 and 13. The Langmuir and Freundlich parameters were determined from their respective plots. Their values are presented in following table. The q_{max} value obtained experimentally and from Langmuir isotherm indicates that the value of q_m for Fe(III) adsorption gradually increases from XAW(5%) to XAW(10%). But the values for the

XAW(15%) and XAW(20%) are almost same. Hence, it can be concluded that the optimized concentration of NaOH for the Xanthation of apple waste is 15%.

Table: 2 Langmuir and Freundlich biosorption isotherm and correlation coefficient with experimental q_{max} for FeIII)

Adsorbent	Langmuir Isotherm			Experimental q_{max}(mg/g)	Freundlich Isotherm		
	q_{max} (mg/g)	B (L/mg)	R^2		K(L/g)	1/n	R^2
XAW(5%)	73.50	0.04	0.96	76.00	30.26	0.34	0.76
XAW(10%)	105.26	0.10	0.99	100.00	14.19	0.40	0.83
XAW(15%)	196.07	0.06	0.99	185.00	24.00	0.41	0.66
XAW(20%)	196.07	0.06	0.99	185.00	17.35	0.49	0.88

The above table also shows that the value of Langmuir equilibrium parameters lies 0 to 1 for the adsorption of Fe(III) on all four XAW. This indicates that equilibrium data fits well with Langmuir isotherm. This is also supported by the fact that the values of correlation coefficient are higher for Langmuir isotherm than for Freundlich isotherm. The table also reveal that the q_{max} value obtained from Langmuir plot for the adsorption of Fe(III) on XAW(15%) and XAW(20%) are exactly same. Hence, the optimized concentration of NaOH for the Xanthation of apple waste is 15%.

Similarly, the Langmuir and Freundlich isotherm parameters for the adsorption of Al(III) on XAW(15%) are presented in below table.

Table: 3 Langmuir and Freundlich biosorption isotherm and correlation coefficient with experimental q_{max} **for Al(III)**

metal	Langmuir isotherm			Experimental	Freundlich isotherm		
	q_{max}(mg/g)	b(L/mg)	R^2	q_{max}(mg/g)	K(L/g)	1/n	R^2
Al(III)	181.81	0.04	0.98	156.00	13.60	0.52	0.88

The q_m value for the Al(III) adsorption on XAW(15%) is 181.81 mg/g. A comparatively high value of correlation coefficient for the Langmuir isotherm indicates that the adsorption process more closely fits to the Langmuir isotherm.

Figures

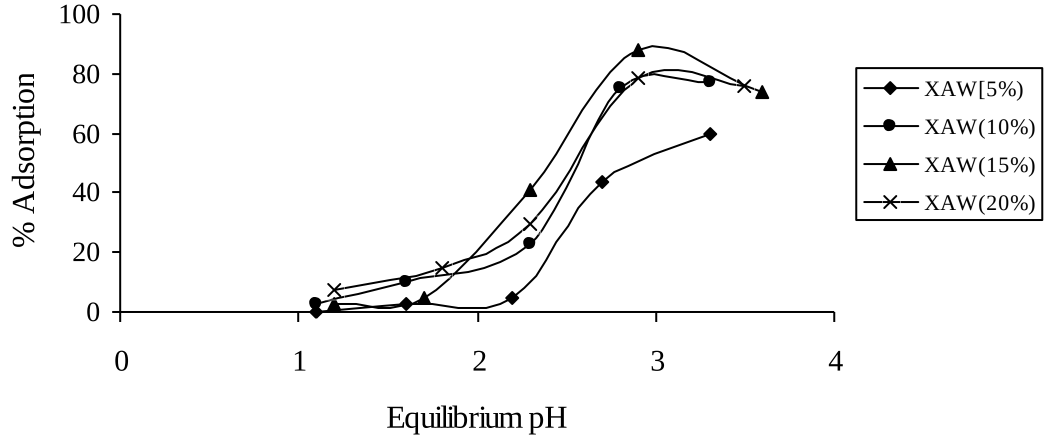

Fig. 8. Effect of pH in the Adsorption of Fe(III) onto Different XAWs.

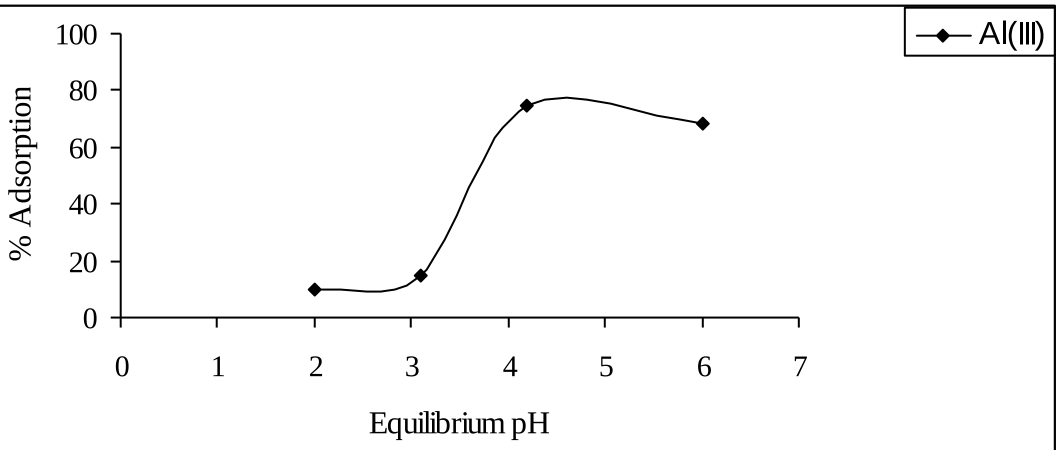

Fig. 9. Effect of pH in the Adsorption of Al(III) onto XAW(15%).

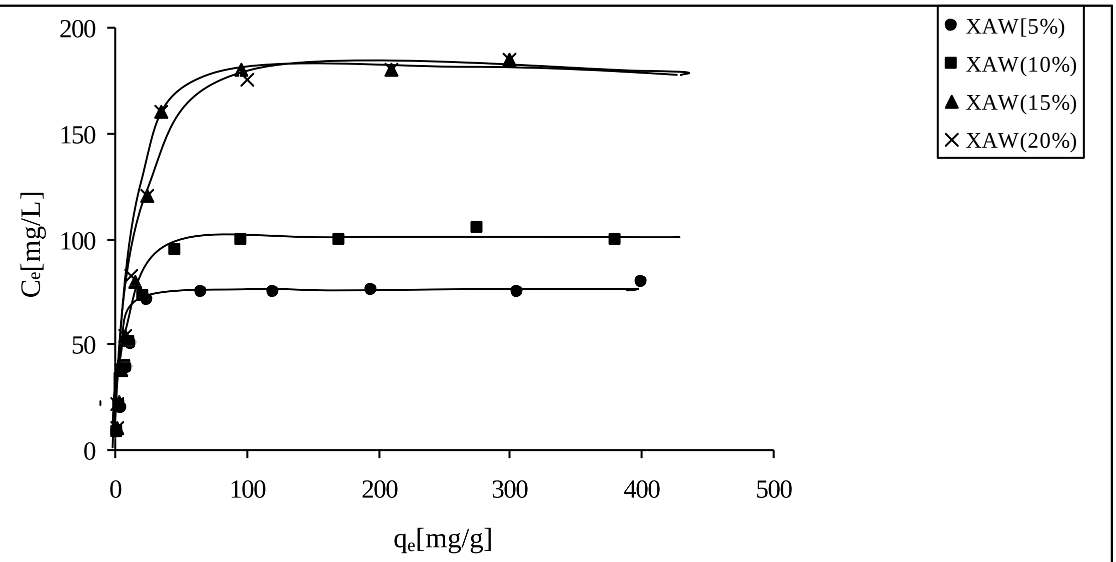

Fig. 10. Adsorption Isotherm in the Adsorption of Fe(III) onto Different XAWs.

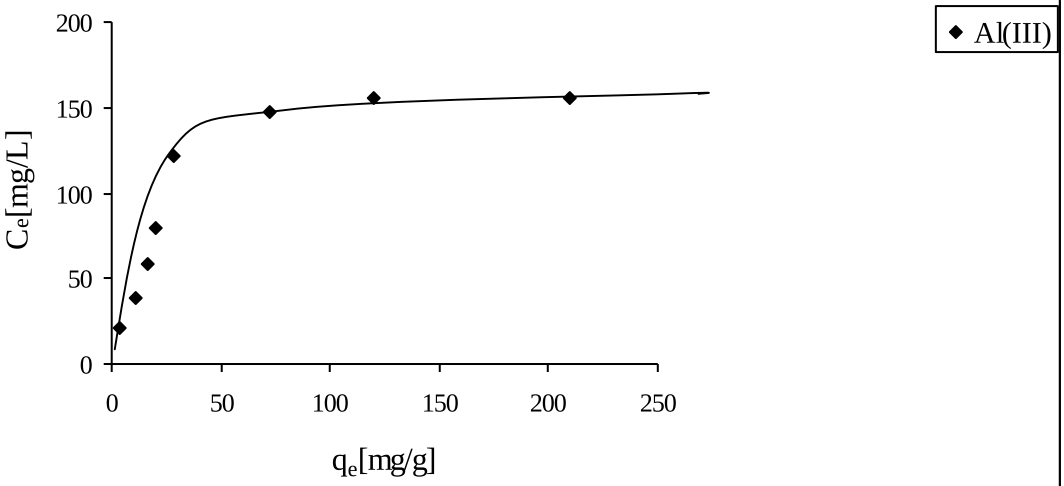

Fig. 11. Adsorption Isotherm in the Adsorption of Fe(III) onto Different XAWs.

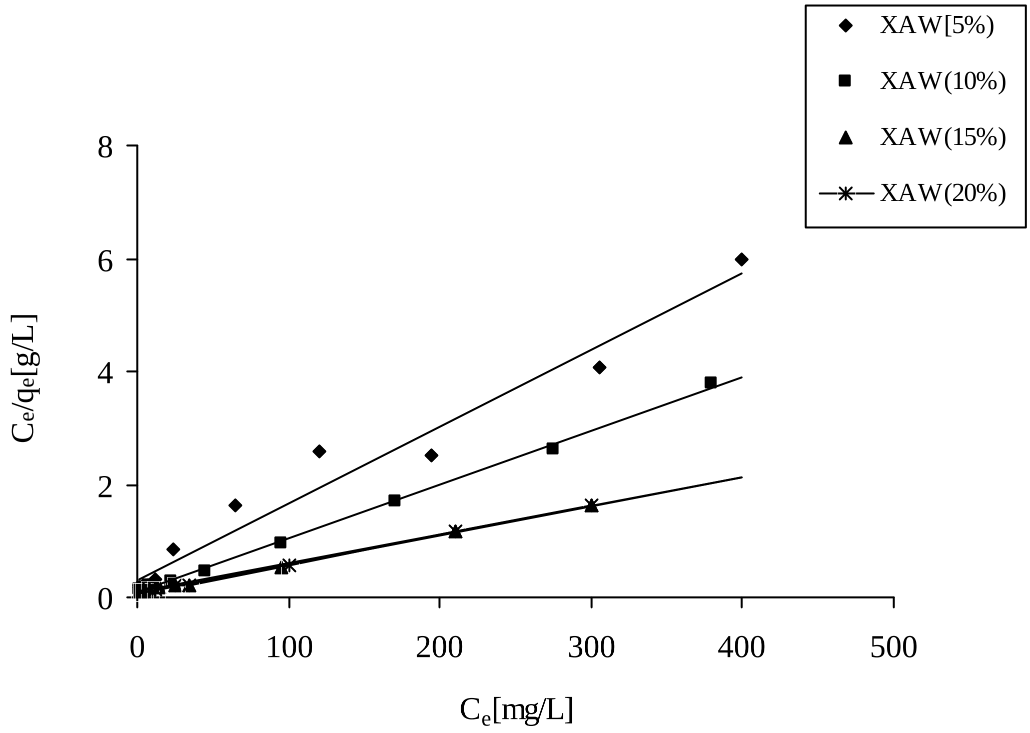

Fig. 12. Langmuir Isotherm Plot for the Adsorption of Fe(III) ions onto Different XAWs.

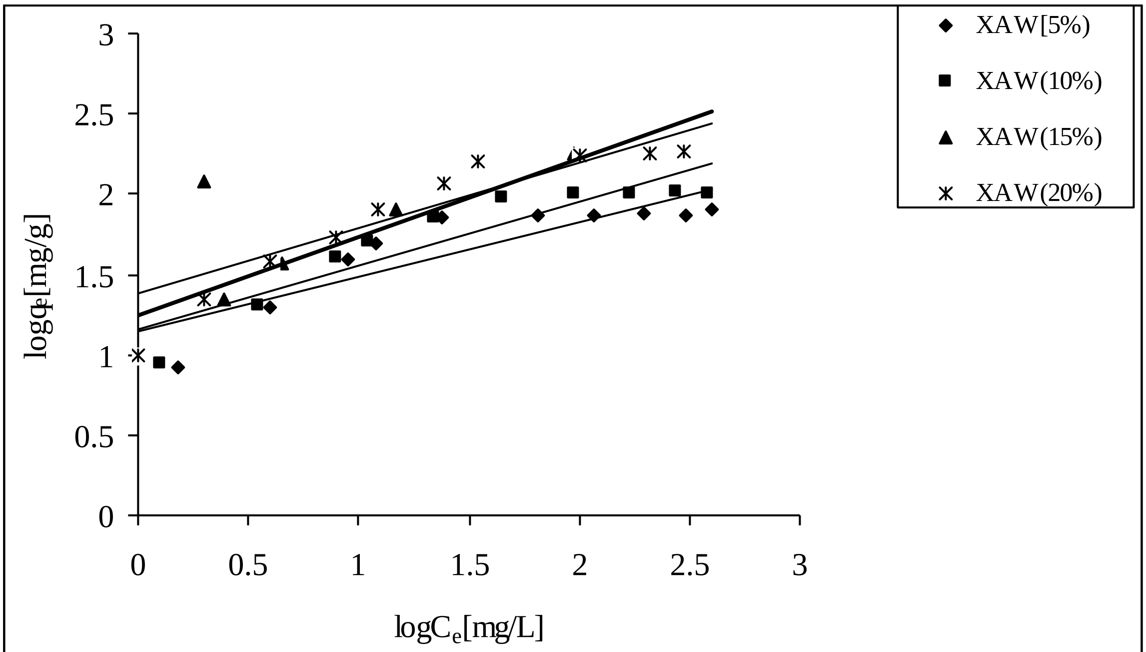

Fig. 13. Freundlich Isotherm for the Adsorption of Fe(III) ions onto Different XAWs

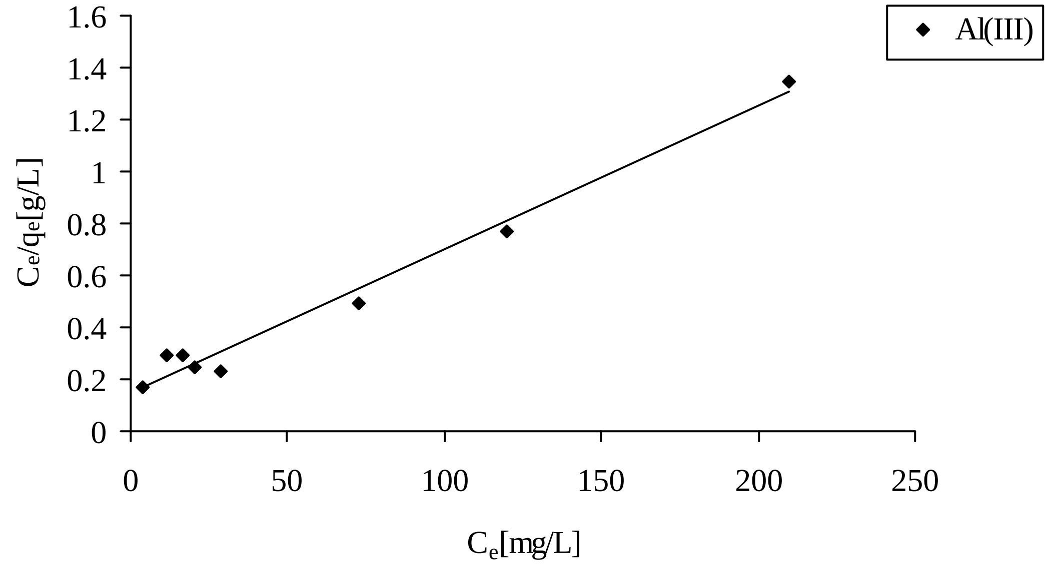

Fig. 14. Langmuir Isotherm for Adsorption of Al(III) ions onto XAW(15%)

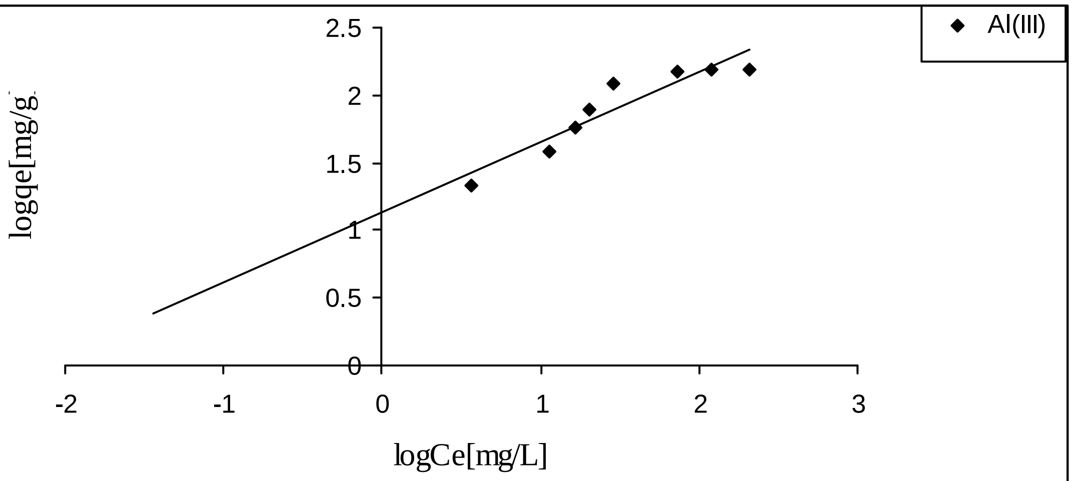

Fig. 15. Freundlich Adsorption Isotherm for the Adsorption of Al(III) ions onto XAW(15%)

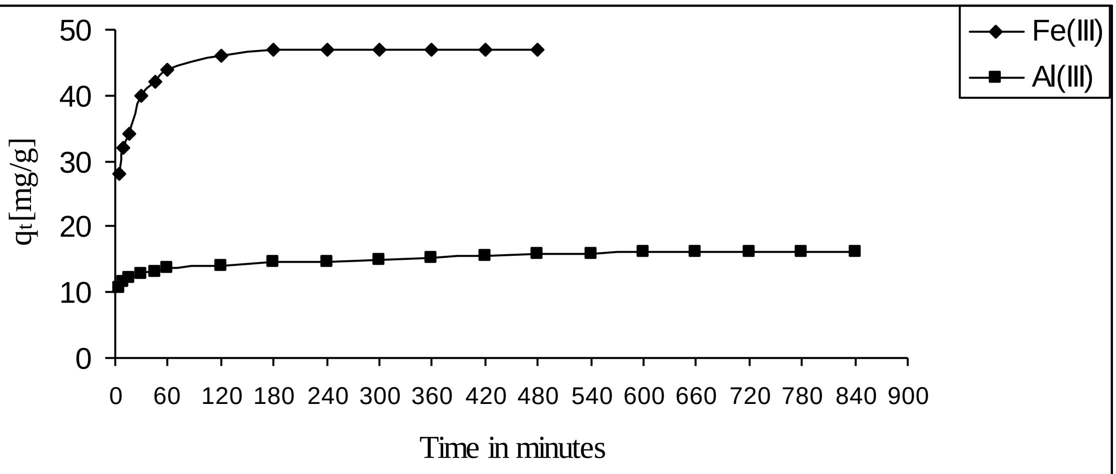

Fig. 16. Effect of Contact Time for the Adsorption of Metal ions onto XAW(15%)

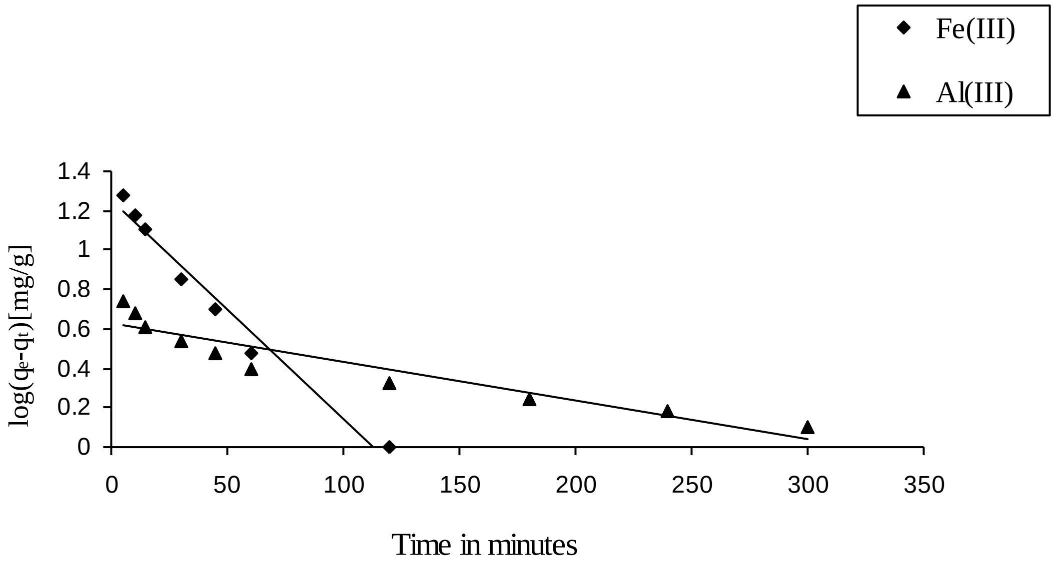

Fig. 17. Pseudo-First Order Kinetic Plot for the Adsorption of Metal ions onto XAW(15%)

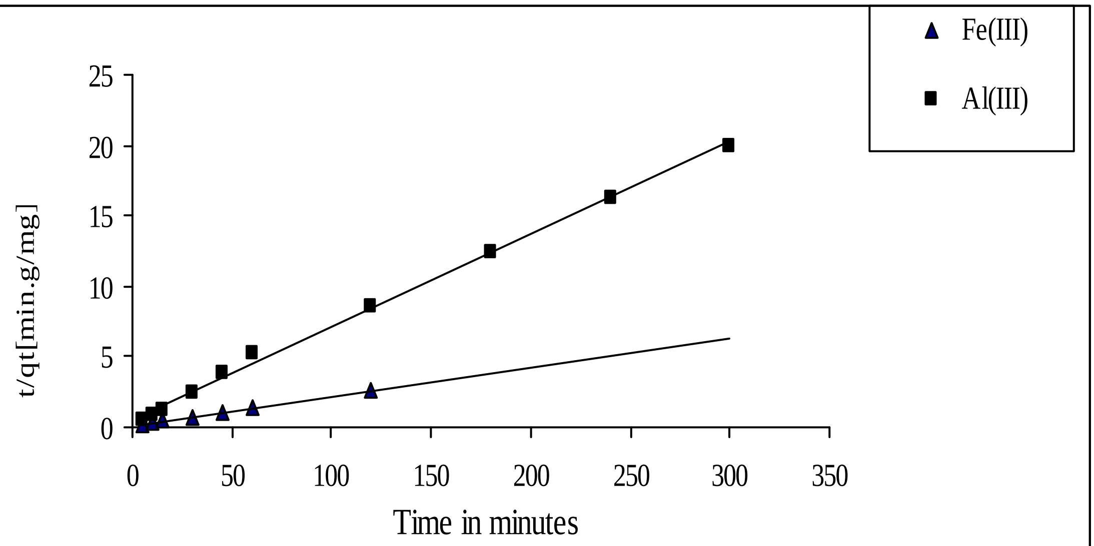

Fig. 18. Pseudo-Second Order Kinetic Plot for the Adsorption of Metal ions onto XAW(15%)

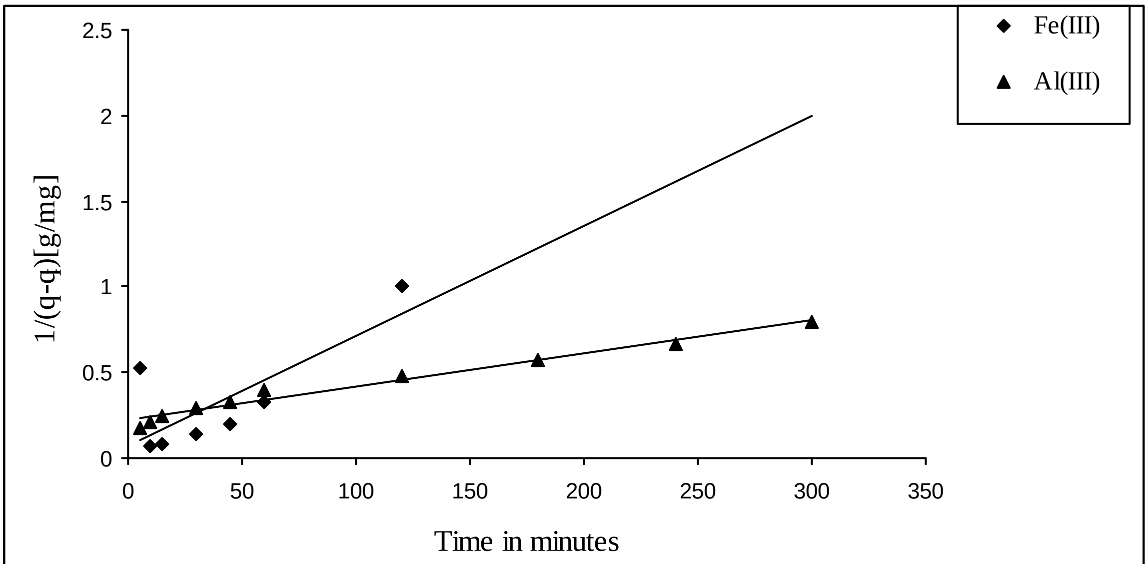

Fig. 19. Second-Order Kinetic Plot for the Adsorption of Metal ions onto XAW(15%)

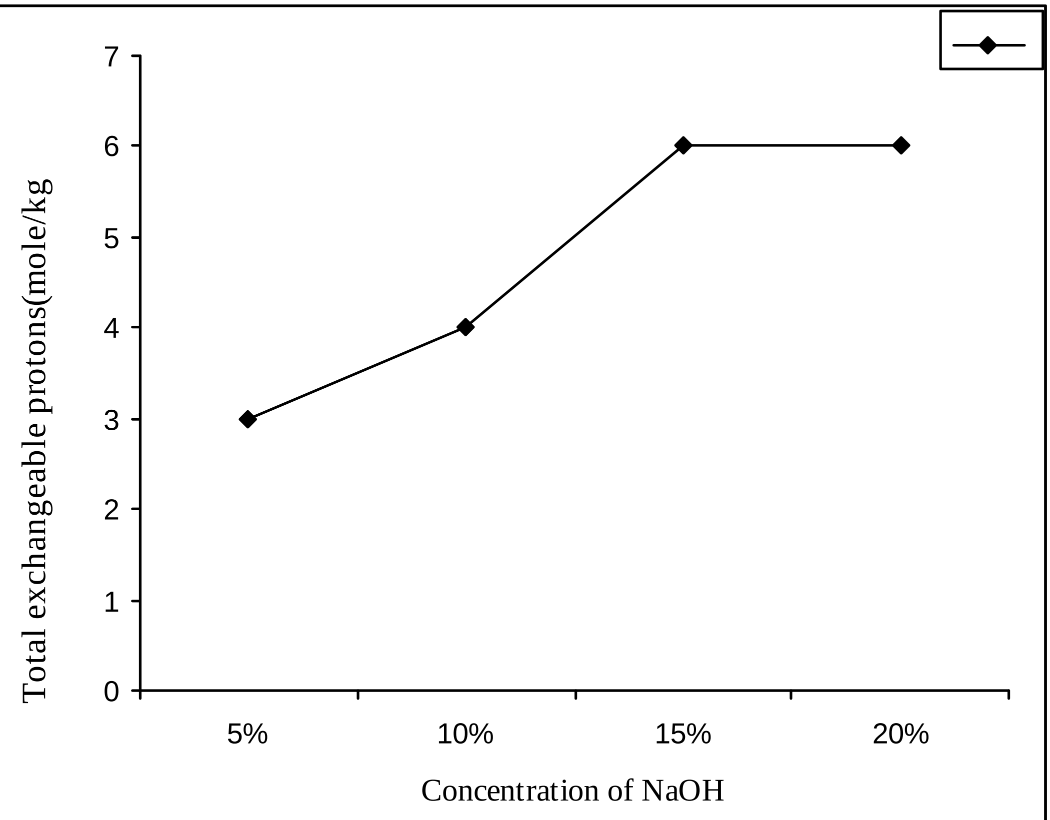

Fig.20. A plot of % of NaOH for Xanthation Vs Total Exchangeable protons on corresponding XAW.

6. Conclusion

In present dissertation work, apple *[pyrus malus]* fruit waste was modified into a more effective adsorbent by Xanthation process in alkaline condition with carbon disulphide. Since the optimized concentration of NaOH was not known for the Xanthation, the Xanthation was carried out with 5%, 10%, 15%, and 20% NaOH concentration. By the evaluation of total exchangeable protons and by the adsorption of Fe(III) on four types of XAW, the optimized concentration of NaOH during xanthation was found to be 15%. The total exchangeable protons were found to be 3 mole/kg, 4 mole/kg, 6 mole/kg and 6 mole/kg for types of XAW, xanthated at 5%, 10%, 15%, and 20% NaOH concentration, respectively. Similarly the maximum iron loading capacity under optimum condition were found to be 73.5 mg/g, 105.26 mg/g, 196.07 mg/gm and 196.07 mg/gm for four XAW, xanthated at 5%, 10%, 15%, and 20% NaOH concentration, respectively. The optimum pH for the adsorption of iron(III) and aluminium(III) was found to be 2.5 and 4.0, respectively.

The maximum adsorption capacity of Al(III) in optimized condition was found to be 170 mg/g. Langmuir and Freundlich isotherm models were tested to describe the adsorption behavior of Fe(III) and Al(III) on XAW and it was investigated that Langmuir model is more suitable than Freundlich model.

The kinetic study for the adsorption of Fe(III) and Al(III) was carried out only with the optimized XAW. The required equilibrium time for the adsorption of Fe(III) and Al(III) was found to be 3 h and 8 h, respectively. The pseudo-first order, pseudo-second order and second order models were tested to analyze the kinetic data. Kinetic studies indicated that pseudo-second order model fitted more than other two models. Hence, the adsorption of Fe(III) and Al(III) onto XAW gel takes place by the pseudo-second order kinetics.

7. Practical Application of XAW

Xanthated Apple waste is one of the effective modified bioadsorbent which can be employed for the adsorption of toxic cations as well as toxic anions after the material is iron loaded. The most important practical application of XAW involves the adsorptive removal of mercury in wastewater. The toxic effect of mercury is due to its high affinity towards the –SH group of protein which may cause the cancer. Since XAW also contain –SH group, it would be specific adsorbent for the adsorptive removal of mercury.

Similarly, the iron loaded XAW can adsorb Arsenic and can be employed for the arsenic treatment which is the burning problem of the Terai region of Nepal. It would be effective, convenient and cost effective technique in the context of Nepal for the Arsenic removal.

8. Limitations of the Study

1. Characterization of the adsorbents was done only by the evaluation of total exchangeable protons.
2. The metal concentration was measured by spectrophotometer which is less sensitive than other modern methods like ICP analysis.
3. Kinetic study was performed at lab temperature and change in adsorption behavior with the change in lab temperature was not considered.
4. The xanthation process was carried with only 5%, 10%, 15%, and 20% NaOH concentration.
5. Adsorption process was studied only with the synthetic solution prepared in the laboratory.
6. Due to unavailability of certified standard metal ion samples, chemicals available in the laboratory were used directly for their respective concentration evaluation with careful attention as mentioned in the standard texts.

9. Suggestion for Further Work

1. The iron loaded XAW can be used for the adsorption of harmful anionic species like phosphate, arsenate, nitrate etc.
2. The xanthated apple waste contain –SH groups. Similarly, Mercury(II) can readily react with –SH group of proteins and may cause cancer. Hence; our adsorbent may be specific for the adsorption of mercury. So adsorption study can be carried out for Hg(II) onto XAW.
3. The xanthation of apple waste was carried out in aqueous alkaline condition and carbon disulphide was insoluble in water. If the xanthation is carried out in the alcohol medium, it would be more effective.
4. XAW can be tested in other heavy metals also.
5. By carrying out adsorption on two different temperatures, the thermodynamic parameters may be obtained.

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Table: 4. Effect of pH in the Adsorption of Fe(III) onto XAW(5%)

Volume of metal solution=20 mL
Concentration of the metal solution=20 mg/L
Amount of adsorbent=20 mg

S.N	Initial pH	Initial Concentration (mg/L)	Equilibrium pH	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	20.5	1.1	20.5	0.0
2	1.5	21.0	1.6	20.5	2.4
3	2.0	20.0	2.2	1.0	5.0
4	2.5	19.5	2.7	21.0	43.5
5	3.0	18.5	3.3	7.5	59.4

Table: 5. Effect of pH in the Adsorption of Fe(III) onto XAW(10%)

Volume of metal solution=20 mL
Concentration of the metal solution=20 mg/L
Amount of adsorbent=20 mg

Initial pH	Initial concentration (mg/L)	Equilibrium pH	Equilibrium concentration (mg/L)	% Adsorption
1.0	19.5	1.1	19.0	2.5
1.5	20.5	1.6	19.5	10.4
2.0	20.0	2.3	15.5	22.5
2.5	20.0	2.8	5.0	75.0
3.0	15.5	3.3	3.5	77.4

Table: 6. Effect of pH in the Adsorption of Fe(III) onto XAW(15%)

Volume of metal solution=20 mL
Concentration of the metal solution=20 mg/L
Amount of adsorbent=20 mg

S.N	Initial pH	Initial concentration (mg/L)	Equilibrium pH	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	20.0	1.2	18.5	7.5
2	1.5	20.5	1.8	17.5	14.6
3	2.0	18.5	2.3	13.0	29.7
4	2.5	18.5	2.9	4.0	78.3
5	3.0	10.5	3.5	2.5	76.0

Table: 7. Effect of pH in the Adsorption of Fe(III) onto XAW(20%)

Volume of metal solution=20 mL
Concentration of the metal solution=20 mg/L
Amount of adsorbent=20 mg

S.N	Initial pH	Initial concentration (mg/L)	Equilibrium pH	Equilibrium concentration (mg/L)	% Adsorption
1	1.0	21.0	1.2	20.5	2.4
2	1.5	21.0	1.7	20.0	4.8
3	2.0	19.5	2.3	11.5	41.0
4	2.5	18.0	2.9	2.0	88.0
5	3.0	11.5	3.6	3.0	73.9

Table: 8. Effect of pH in the Adsorption of Al(III) onto XAW(15%)

Volume of metal solution=20 mL
Concentration of the metal solution=10 mg/L
Amount of adsorbent=20 mg

S.N	Initial pH	Initial concentration (mg/L)	Equilibrium pH	Equilibrium concentration (mg/L)	% Adsorption
1	2.0	10.0	2.0	9.0	10.0
2	3.0	10.0	3.1	8.5	15.0
3	4.0	9.5	4.2	2.5	75.0
4	5.0	4.0	6.0	1.2	68.0

Table: 9. Effect of Concentration in the Adsorption of Fe(III) onto XAW(5%)

(20 mL solution of Fe(III) with 20 mg adsorbent)
Optimum pH 2.5

S.N	Initial concentration C_i(mg/L)	Equlibrium concentration C_e(mg/L)	Amount of Fe(III) adsorbed q_e(mg/g)	C_e/q_e (L/g)	logC_e (mg/L)	logq_e (mg/g)
1	10.0	1.5	8.5	0.17	0.18	0.92
2	24.0	4.0	20.0	0.20	0.60	1.30
3	42.0	9.0	39.0	0.24	0.95	1.59
4	62.0	12.0	50.0	0.33	1.08	1.69
5	95.0	24.0	71.0	0.86	1.38	1.85
6	140.0	65.0	75.0	1.63	1.81	1.87
7	195.0	120.0	75.0	2.60	2.07	1.87
8	270.0	194.0	76.0	2.52	2.29	1.88
9	380.0	305.0	75.0	4.06	2.48	1.87
10	480.0	400.0	80.0	6.00	2.60	1.90

Table: 10. Effect of Concentration in the Adsorption of Fe(III) onto XAW(10%)

(20 mL solution of Fe(III) with 20 mg adsorbent)
Optimum pH 2.5

S.N	Initial concentration C_i(mg/L)	Equlibrium concentration C_e(mg/L)	Amount of Fe(III) adsorbed q_e(mg/g)	C_e/q_e (L/g)	logC_e (mg/L)	logq_e (mg/g)
1	10.0	1.2	8.8	0.14	0.10	0.94
2	24.0	3.5	20.5	0.17	0.54	1.31
3	42.0	8.0	40.0	0.20	0.90	1.60
4	62.0	11.0	51.0	0.22	1.04	1.70
5	95.0	22.0	73.0	0.30	1.34	1.86
6	140.0	45.0	95.0	0.47	1.65	1.98
7	195.0	95.0	100.0	0.95	1.98	2.00
8	270.0	170.0	100.0	1.70	2.23	2.00
9	380.0	275.0	105.0	2.62	2.44	2.02
10	480.0	380.0	100.0	3.80	2.58	2.00

Table: 11. Effect of Concentration in the Adsorption of Fe(III) onto XAW(I5%)

(20 mL solution of Fe(III) with 20 mg adsorbent)
Optimum pH 2.5

S.N	Initial concentration C_i (mg/L)	Equlibrium concentration C_e(mg/L)	Amount of Fe(III) adsorbed q_e(mg/g)	C_e/q_e (L/g)	logC_e (mg/L)	logq_e (mg/g)
1	11.0	1.0	10.0	0.10	0.00	1.00
2	24.0	2.5	22.5	0.11	0.39	1.35
3	42.0	4.5	37.5	0.12	0.65	1.57
4	62.0	8.0	54.0	0.13	0.90	1.73
5	95.0	15.0	80.0	0.19	1.17	1.90
6	145.0	25.0	120.0	0.20	0.30	2.08
7	195.0	35.0	160.0	0.22	1.54	2.20
8	275.0	95.0	180.0	0.53	1.98	2.25
9	390.0	210.0	180.0	1.17	2.32	2.25
10	485.0	300.0	185.0	1.62	2.47	2.26

Table: 12. Effect of Concentration in the Adsorption of Fe(III) onto XAW (20%)

(20 mL solution of Fe(III) with 20 mg adsorbent)

Optimum pH 2.5

S.N	Initial concentration C_i(mg/L)	Equlibrium concentration C_e(mg/L)	Amount of Fe(III) adsorbed q_e(mg/g)	C_e/q_e (L/g)	logC_e (mg/L)	logq_e (mg/g)
1	11.0	1.0	10.0	0.10	0.00	1.00
2	24.0	2.0	22.0	0.09	0.30	1.34
3	42.0	4.0	38.0	0.10	0.60	1.58
4	62.0	8.0	54.0	0.14	0.90	1.73
5	95.0	12.5	82.5	0.15	1.09	1.91
6	145.0	25.0	120.0	0.20	1.39	2.07
7	195.0	35.0	160.0	0.22	1.54	2.20
8	275.0	100.0	175.0	0.57	2.00	2.24
9	390.0	210.0	180.0	1.17	2.32	2.25
10	485.0	300.0	185.0	1.62	2.47	2.26

Table: 13. Effect of Concentration in the Adsorption of Al(III) onto XAW(15%)

(20 mL solution of Al(III) with 20 mg adsorbent)

pH=4.0

S.N.	Initial concentration C_i(mg/L)	Equlibrium concentration C_e(mg/L)	Amount of Al(III) adsorbed q_e(mg/g)	C_e/q_e (L/g)	logC_e (mg/L)	logq_e (mg/g)
1.	25.0	3.7	21.3	0.17	0.56	1.33
2.	50.0	11.2	38.8	0.29	1.05	1.59
3.	75.0	16.8	58.2	0.29	1.22	1.76
4.	100.0	20.5	79.5	0.25	1.31	1.90
5.	150.0	28.8	121.2	0.23	1.46	2.08
6.	220.0	72.5	147.5	0.49	1.86	2.17
7.	275.0	120.0	155.0	0.77	2.08	2.19
8.	368.0	210.0	156.0	1.35	2.32	2.19

Table: 14. Kinetics Study of Aluminium onto XAW(15%)

pH=4.0
Volume of solution taken=20 mL
Concentration of the solution=25 mg/L
Amount of adsorbent=20 mg

S.N	Time in min	C_t (mg/L)	q_t (mg/g)	q_e-q_t (mg/g)	1/(q_e-q_t) (g/mg)	log(q_e-q_t) (mg/g)	t/q (min.g/mg)
1.	5	14.25	10.75	5.50	0.18	0.74	0.47
2.	10	13.50	11.50	4.75	0.21	0.68	0.87
3.	15	12.80	12.20	4.05	0.25	0.61	1.23
4.	30	12.25	12.75	3.50	0.29	0.54	2.45
5.	45	11.75	13.25	3.00	0.33	0.48	3.83
6.	60	11.25	13.75	2.50	0.40	0.40	5.33
7.	120	10.85	14.15	2.10	0.48	0.32	8.48
8.	180	10.50	14.50	1.75	0.57	0.24	12.41
9.	240	10.25	14.75	1.50	0.67	0.18	16.27
10.	300	10.00	15.00	1.25	0.80	0.10	20.00
11	infinite	8.75	16.25 (q_e)	0.00	-	-	

Table: 15. Kinetic Data for Adsorption of Fe(III) onto XAW(15%)

Total volume (V) - 20 mL.
Amount of adsorbent (W) - 20 mg.
Initial metal concentration (C_i) - 52 mg/L
pH – 2.5

S.N	Time in min	C_t(mg/L)	q_t (mg/g)	q_e-q_t (mg/g)	1/(q_e-q_t) g/mg	log(q_e-q_t) (mg/g)	t/q_t (min.g/mg)
1.	5	24	28	19	0.53	1.28	0.18
2.	10	20	32	15	0.07	1.18	0.31
3.	15	18	34	13	0.08	1.11	0.44
4.	30	12	40	7	0.14	0.85	0.75
5.	45	10	42	5	0.20	0.70	1.07
6.	60	8	44	3	0.33	0.48	1.36
7.	120	6	46	1	1.00	0.00	2.60
8.	infinite	5	47(q_e)	-	-	-	-

Table:16. Effect of Contact Time for the Adsorption of Fe(III) onto XAW(15%)

Volume of metal solution=20 mL
Initial concentration=52 mg/L
Mass of the adsorbent=20 mg
pH=2.5

S.N	Time in min	Concentration at time, t (mg/L)	q_t (mg/ g)
1.	5	24	28
2.	10	20	32
3.	15	18	34
4.	30	12	40
5.	45	10	42
6.	60	8	44
7.	120	6	46
8.	180	5	47
9.	240	5	47
10.	300	5	47
11.	360	5	47
13.	420	5	47
14.	480	5	47

Table: 17. Effect of Contact Time for the Adsorption of Al(III) onto XAW(15%)

Volume of metal solution=20 mL
Initial concentration=25 mg/L
Mass of the adsorbent=20 mg
pH=4.0

S.N	Time (min)	Concentration at time t (mg/L)	q_t (mg/g)
1.	5	14.25	10.75
2.	10	13.50	11.50
3.	15	12.80	12.20
4.	30	12.25	12.75
5.	45	11.75	13.25
6.	60	11.25	13.75
7.	120	10.85	14.15
8.	180	10.50	14.50
9.	240	10.25	14.75
10.	300	10.00	15.00
11.	360	9.75	15.25
13.	420	9.50	15.50
14.	480	9.25	15.75
15.	540	9.00	16.00
16.	600	8.75	16.25
17.	660	8.75	16.25
18..	720	8.75	16.25
19.	780	8.75	16.25
20.	840	8.75	16.25

Table: 18. Finding of λ_{max} for Spectrophotometric Determination of Fe(II)

S.N	Wavelength(nm)	Absorption(O.D)
1	400	.23
2	425	.30
3	450	.40
4	475	.46
5	500	.48
6	505	.49
7	510	.47
8	515	.46
9	525	.42
10	550	.14

Table: 19. Construction of Calibration Curve for Fe(III)

S.N	Concentration(mg/L)	Absorbance(O.D)
1	1	.09
2	2	.2
3	3	.3
4	4	.4
5	5	.5
6	6	.6
7	7	.7
8	8	.8
9.	9	.9

Table: 20. Finding of λ_{max} for Spectrophotometric Determination of Al(III)

S.N.	Wavelength(nm)	Absorption(O.D)
1.	400	0.11
2.	425	0.09
3.	450	0.11
4.	475	0.16
5.	500	0.34
6.	525	0.80
7.	530	0.78
8.	535	0.65
9.	540	0.52
10.	550	0.40
11.	575	0.21
12.	600	0.08

Table: 21. Construction of Calibration Curve for Al(III)

S.N	Concentration of Al(III) in (µg/L)	Absorption(O.D)
1.	25	0.05
2.	50	0.11
3.	75	0.17
4.	100	0.22
5.	150	0.33
6.	200	0.44
7.	250	0.55
8.	300	0.66
9.	400	0.87

Table: 22
Accuracy and Precision of the Spectrophotometric Method for the Determination of Iron(III) by 1, 10-phenonthroline

S.N.	Amount of iron taken (μg)	Abs.	Amount of iron found (μg)	Mean	Standard Deviation	95% Confidence Interval
1.	25.0	0.09	22.5	24.375	1.25	24.375±1.99
	25.0	0.10	25.0			
	25.0	0.10	25.0			
	25.0	0.10	25.0			
2.	50.0	0.20	50.0	49.375	1.25	49.375±1.99
	50.0	0.20	50.0			
	50.0	0.20	50.0			
	50.0	0.19	47.5			
3.	75.0	0.30	75.0	74.375	1.25	74.375±1.99
	75.0	0.30	75.0			
	75.0	0.29	72.5			
	75.0	0.30	75.0			
4.	100.0	0.40	100.0	99.375	1.25	99.375±1.99
	100.0	0.40	100.0			
	100.0	0.40	100.0			
	100.0	0.39	97.5			

Table: 23

Accuracy and Precision of the Spectrophotometric Method for the Determination of Aluminium(III) by Eriochrome Cyanine R

S.N.	Amount of Al(III) taken (µg)	Abs.	Amount of Al(III) found (µg)	Mean	Standard Deviation	95% Confidence Interval
1.	1.25	0.11	1.25	1.25	0.102	1.25±0.162
	1.25	0.11	1.25			
	1.25	0.12	1.37			
	1.25	0.10	1.12			
2.	2.50	0.23	2.62	2.50	0.102	2.50±0.162
	2.50	0.22	2.50			
	2.50	0.22	2.50			
	2.50	0.21	2.37			
3.	5.00	0.44	5.00	5.00	0.102	5.00±0.162
	5.00	0.44	5.00			
	5.00	0.45	5.12			
	5.00	0.43	48.75			
4.	7.50	0.66	7.50	7.50	0.102	7.50±0.162
	7.50	0.66	7.50			
	7.50	0.65	7.37			
	7.50	0.67	7.62			