

Biosorption of Hg²⁺ ions by Sulphonated biomass of Stalks of *Prunus cerasus*

ANANDRAO A. KALE^{1*}

^{1*}. Post Graduate department and Research Centre of Chemistry

Annasaheb Awate College, Manchar, Tal. Ambegaon. Dist-Pune, (Maharashtra)

Corresponding author A. A. Kale ^{1}: E Mail- anandraoakale@gmail.com

ABSTRACT

The biosorption of Hg²⁺ ions by Sulphonated biomass of *Stalks of Prunus cerasus* carried out in batch conditions. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been carried out. The kinetic study of biosorption results shows that sorption process is well explained by pseudo-second order model with determination coefficients higher than 0.94 for sorbent under all experimental conditions. A 5 gm dose of shows maximum adsorption is about 65%.; Optimum pH for adsorption of Sulphonated biomass of Hg²⁺ Stalks of *Prunus cerasus* found to be pH 7. The K_f values for Stalks of *Prunus cerasus* are 45.11 and 46.2, indicating good adsorption follows the Freundlich model. The K₂ values for Stalks of *Prunus cerasus* is 0.699, with R² 0.99. Thermodynamic parameter via KD, ΔG has also been calculated to determine the spontaneity of the process. The value K_p is found to be 0.60 to 2.50 for initial and final concentrations. The Kinetic modeling indicates that the adsorption follows pseudo second order kinetics. The low value of activation energy indicates that sorption is an activated and physical process. Thus sulphonated biomass of Stalks of *Prunus cerasus* a low cost and easily available efficiently used as an excellent sorbent for the removal of Hg²⁺ ions.

Key words: biosorbent, adsorption isotherm, E.D.T.A., Sulphonated biomass of *Stalks of Prunus cerasus*.

INTRODUCTION

The heavy metals in waste water as well as industrial effluents have emerged as the focus of environmental remediation effort because of their toxicity to human being. The processes adsorption is found to be highly effective, cheap and easy method. Active carbon in most cases has been used as adsorbent for reclamation of municipal and industrial waste water for almost last few decades but the high cost carbon has inspired investigation to search for low cost agriculture waste as adsorbents. The ground water is mainly contaminated by heavy metals released from industrial and their persistence in food chain has been of major concern as it is seriously poisoning aquatic culture including fisheries. The heavy metal Hg²⁺ present in high concentration in the waste of industries like pharmaceutical, paint, pigment, insecticide,

cosmetics and polymer etc. causes serious problems to environment. The Hg^{2+} reported by WHO is highly toxic to human life, and other heavy metals are reported to be bio-accumulated into flora and fauna creating ecological problems. The toxicity of hexavalent chromium from the discharge of various industrial wastes is well studied by D.K. Singh [1]. The use of various adsorbent such as activated carbon, rice husk carbon saw dust, and fly ash, ash- woolastonite have also been documented for the removal of Cr (VI) from aqueous solutions. Srivastava et al have studied adsorption of heavy metal ions on carbonaceous material developed from waste slurry of fertilizer plants, Biosorption of Chromium (VI) from aqueous solutions by the husk of Bengal gram [2] (*Cicer arietinum*), Subramaniam K.S. et al have reported mercury [3] contamination of drinking water and utilization of fly ash and waste tea leaves as decolorizing agent for dye effluents. Periasamy and Namasivaym used the agricultural waste activated carbons reported that the carbons prepared from the waste are successfully employed for the removal of Ni (II) from waste water [4]. Marshall and Johns evaluated the sorption properties of deflated rice bran, soya bean and cotton seed hulls and their resistance to mechanical abrasion[5]. Othman and Amen have used the rhizopus oligosporus biomass for the biosorption of Cu^{2+} , Mn^{4+} , Zn^{2+} at the maximum adsorption rate [6]. Li Q., Wu, S. et al. worked on comparison between biosorption of Hg^{2+} ions and Cd^{2+} by the biomass of *P. Chrysosporium*[7]. Ricardo. C., Tarley and Arruda characterized the rice milling by-products [8], used for removing Cd (II) and Pb (II) ions from effluents. Biosorption of nickel (II) and Copper (II) ions from aqueous solution by dried *Streptomyces colicolor* Al (II) [9] was studied by Ozturk et. al. as a function of concentration, pH and temperature. Mirtezky et. al. studied the mechanism of simultaneous metal removal Cd (II), Ni(II), Cu(II), Zn(II) and Pb(II) by three macrophyte biomass [10]. Partially converted crab shell waste which contains chitosan was used by Pradhan et.al to remove nickel from water. [11]. Padmavathy et.al. worked on the biosorption of nickel (II) ions by deactivated protonated yeast. [12]. Akar et.al. carried out a study on Hg^{2+} accumulation on the surface of *Botrytis cinerea* [13]. The biosorption of cadmium and mercury ion from artificial aqueous solution using waste baker's yeast biomass [14] was investigated by Goksungur et al. Choy and McKay studied the rate of adsorption of cadmium [15], copper and zinc ions onto bone char in three single component systems using an agitated batch adsorbent Rice straw soybean hull, sugar baggase. Adsorption behavior of Cd^{2+} , Hg^{2+} , Ni^{2+} , Cd^{2+} and Zn^{2+} from aqueous solutions by *mangifera indica*[16] a seed shell was reported by Mohammad Ajmal and et al. , Tsunetaka Sasaki and et al. has been worked on adsorption of dyes, chromate and metallic ions by poly(ethyleneimine[17]), Removal of Fe^{2+} , Zn^{2+} and Mg^{2+} from polluted water using thioglycolic modified oil-palm fiber[18] was done by J.O.Akaniwor and et al. Mazahar Farooqui reported that the use leaves of Cauliflower [19] for removal of iron from waste water. Badie S. Girgis and et al has been worked on activated carbon from cotton stalks [20] by impregnation with phosphoric acid. A Sorption study of Al^{3+} , Co^{2+} and Ag^{+} in aqueous solutions by Fluted Pumpkin [21] waste biomass was carried out by Michael Horsfull Jnr and Ayebaemi I. Spiff. The uptake capacity of Chromium (VI) by sulphonated and sulphonated Coconut Shell carbon [22] was studied by V. Selvi and G.P. Jeyanthi, A batch study was carried out by Mohamed Chaker Ncibi and et al. on biosorption of textile dyes [23] from aqueous solutions using *Posidonia oceanica* leaf sheath fibers. In the recent years the activities of industrial sectors has showed a considerable spread and development, but concurrently the natural environment has been contaminated. The toxicity of hexavalent chromium from the discharge of various industrial wastes is well studied by D.K. Singh [1]. A number of industries are causing heavy metal pollution e.g. battery manufacturing processes,

mining and metallurgical engineering, dyeing operations, electroplating, nuclear power plants, tanning, production of paints and pigments [24]. Heavy metals are one of the most widespread pollutants which contaminate the environment and cause serious damage to the ecosystem and also may be a reason for various dangerous diseases suffered by animals and human beings [25]. Chromium [Cr] compounds are among the most common environmental contaminants because of their widespread and extensive use in industrial applications [26]. Chromium (VI) is more toxic than chromium (III) and as such receives more attention. Strong exposure to chromium (VI) has been linked to various types of cancer and may cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [27]. Chromium (VI) is one of the most poisonous contaminants which cause severe diseases and very harmful environmental complications. When chromium (VI) accumulates at high levels, it may mercury to serious problems and even be fatal when concentrations reach 0.10 mg/g of body mass [28]. The removal of toxic metals from wastewater has been achieved using various methods sedimentation [29], ion exchange [30], biological operations [31], solid phase extraction [32], and adsorption by chemical substance [33]. Several conventional physical, chemical, and biological methods have been developed to remediate Cr (VI)-contaminated wastewater and water, and thereby avoid or reduce the adverse effects of highly toxic Cr (VI) on human health and the environment [34]. All these techniques suffer from multiple drawbacks such as high capital and operational costs and disposal of residual metal sludge [35].

EXPERIMENTAL

Preparation of biosorbent Stalks of *Prunuscerasus*:

The sieved biomass of *Stalks of Prunuscerasus* was taken in a beaker and soaked in AR conc. sulphuric acid for 1 hour. The mass was then heated on a water bath till the brown fumes ceased. It was then washed thoroughly with distilled water till the brown black mass was acid free. It was then dried at 110 °C in the oven for 3 hours. The dried material was then passed through 0.63 mm mesh get particles of uniform size. The present work deals with the study of adsorption of heavy metals Hg²⁺ ions on chemically treated biomass of *Stalks of Prunuscerasus*.

Adsorption experiments were carried out for adsorption of mercury using sorbents **Stalks of Prunuscerasus**. A standard solution of HgCl₂ of strength 0.00202 gm Hg²⁺/ml. was prepared (solution A). To the 50 ml of solution A exactly 50 ml of distilled water were added in a conical flask maintained at constant temperature in a thermostat. To this 500 mg of the appropriate sorbent *Stalks of Prunuscerasus* was added, it was stirred for 2.5 minutes and then filtered. The same procedure was followed for time intervals 5.0, 7.5, 10, 15, 30, 90, 120, and 180 minutes. Similar experiments were repeated using different material doses 1.0 gm, 2.0 gm, 5.0 gm. Amount of mercury in the filtrate was determined by titrating against standardized E.D.T.A. The effect of contact time, temperature, pH of solution, and material dose on removal of the Hg²⁺ ion was studied. (All Chemicals used Merck Chem.).

Sorption Kinetics

Uptake capacity was calculated from the mass balance as follows

$$q = \frac{(C_0 - C_t) V}{100 W}$$

Where q is the quantity of sorbate (dye or metal) uptake by biomass, C_0 and C_t are the initial and final concentrations respectively. V is the volume of solution in ml and W is the dry weight of the biomass added. Calibration and actual experiments were carried triplicate and mean values are presented.

RESULT AND DISCUSSION

Characterization of biosorbents.

The physical parameter and I R spectrum data of **Stalks of Prunuscerasus** is described in Table-1.

Table- 1

Adsorbent	Bulk density g / cc	Moisture content %	Ash Content %	Volatile material %
Stalks of Prunuscerasus	0.32	2.75	3.23	5.9

I R spectrum data for Sorbent Sulphonated biomass of Stalks of Prunuscerasus (S-III) indicate 3350 cm^{-1} broad -OH , 3025 cm^{-1} -NH , 1720 cm^{-1} COOH

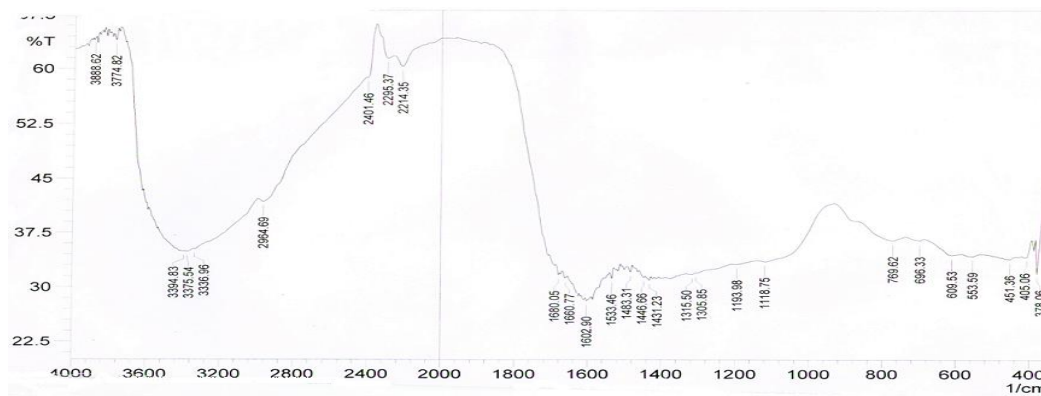


Fig.1 Infra Red Spectrum of biosorbent (Stalks of Prunuscerasus)

Sorption Kinetic Models

Percentage removal analysis of sorption data: The removal percentage is calculated by equation $PR (\%) = [1 - C_e/C_0] \times 100$

Where PR % = removal percentage of dye or metal ion from static system after agitation C_0 = of initial metal ion concentration, C_t with fixed dosage of adsorbent and C_e = sorbate concentration at experimental equilibrium stage.

Langmuir isotherm model:

Langmuir isotherm was applied for adsorption equilibrium data. The Langmuir isotherm is based on the following assumptions:

- Adsorbate / metal ions are chemically adsorbed at fixed number of well – defined sites
- each site can hold only one ion
- All sites are energetically equivalent; and There is no interaction between adsorbed ions. When the initial sorbate concentration increases adsorption increases whilst the binding sites are not saturated. The unmodified Langmuir equation is as follows

$Q_e = \frac{abC_e}{1+bC_e}$ Where a= maximum adsorption capacity (mg/g)

b = Langmuir isotherm parameter related to the energy of adsorption (1/mg)

Freundlich isotherm model: Freundlich equation is used for heterogeneous surface energy term. Freundlich isotherm can also be used to explain adsorption phenomenon as given:

$$Q_e = K_f C_e^{1/n}$$

The linearized Freundlich model isotherm is represented by equation

$$\log_{10} q_e = \log_{10} K_f + \frac{1}{n} \log_{10} C_e$$

Where, K_f and n are constants incorporating all factors affecting the adsorption capacity and an indication of the favorability of metal ion adsorption onto carbon respectively.

Adsorption thermodynamic equation: Value of the thermodynamic parameter free energy ΔG° were calculated using following thermodynamic equation (Sarin and Pant, 2006)

$\Delta G^\circ = -RT \ln K$; where ΔG° change in free energy (KJ/mol); T = Absolute temperature (K) , R (Universal gas constant) = 8.314 J/mole . K; K is the equilibrium constant at temperature, T The equilibrium constant, K can be calculated from. $K = q_e/C_e$

Kinetic models:

Kinetics of adsorption on Sulphonated biomass of sorbent Stalks of *Prunus cerasus* can be modeled by the pseudo first order Lagergren equation and Pseudo second order model. The rate constant of adsorption from the first order rate expression. $\log(q_e - q_t) = \log q_e - (K_1/2.303) t$

Where q_e and q are the amount of dye adsorbed (mg/g) at equilibrium and K_1 is the rate constant. The second-order kinetics model is expressed as $t/q = 1/k_2 q_e^2 + t/q_e$

The initial adsorption rate (mg/g) to can be defined as $n = k_2 q_e^2$

The initial adsorption rate (h) equilibrium adsorption capacity (q_e) and 2nd order rate constant K_2 (g/mg min) are determined experimentally, from the slope and intercept of the plot.

Intra particle diffusion study: Adsorption by porous particles is a process which involves a number of steps. The most common empirical function which explains adsorption is that the uptake varies almost proportionally with $t^{1/2}$ and rather than contact time. $Q_t = k_i d^{1/2} t^{1/2} + C$

According to the equation the plot of q_t vs. $t^{1/2}$ should be a straight line passing through origin, when the intraparticle diffusion is the rate controlling step. If the plot of q_t vs. $t^{1/2}$ is non linear it indicates the adsorption is not governed by a single mechanism.

Effect of time on adsorption of Hg²⁺ by Stalks of *Prunus cerasus*

A study of effect of time on adsorption of mercury (Hg²⁺ ion) shows that with increase in time the adsorption increases and equilibrium is attained after 2 hours. **Fig.2** Uptake of mercury at equilibrium time two hours for 500 mg is 27.0 %. The % adsorption of Hg²⁺ ion from its solution of concentration 200 mg/dm³ was found to be 58.7 %

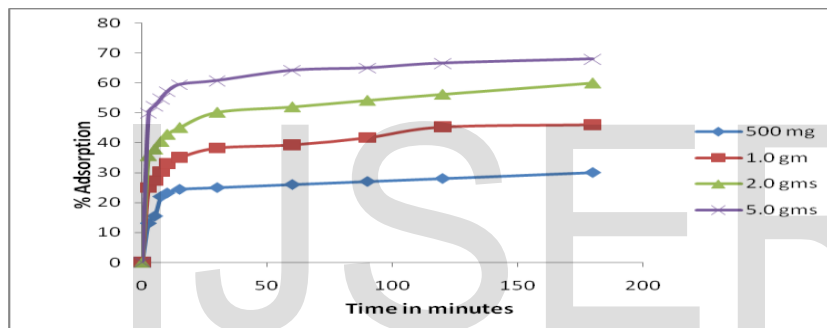


Fig. -2 Effect of time on % adsorption by Stalks of *Prunus cerasus*

Effect of material dose:

The uptake capacity of any adsorbing material increases with increase in the dose as more sites are available for adsorption on the sorbent. The trends in adsorption of Hg²⁺ ions on **Stalks of *Prunus cerasus*** are increased with increasing the biomass dose. For **Stalks of *Prunus cerasus*** the x/m value falls from 49.2 mg/g to 9.89 mg/g. Increase in the material dose from 500 mg to 5 gm/100 ml shows increase in % adsorption but a decrease in adsorption capacity. (Fig. 3) A fixed amount of sorbent has a fixed number of sites for adsorption; amount increases the total number of sites available for adsorption increase. When a solution comes in contact with the larger mass of sorbent the Hg²⁺ ions rapidly interact with maximum sites on the surface. This mercury to a reduced population of the metal ions per unit mass of the sorbent compared to that when a smaller mass of sorbent is used. Effectively we find that percentage adsorbed has increased but the amount adsorbed per unit mass of sorbent has reduced.

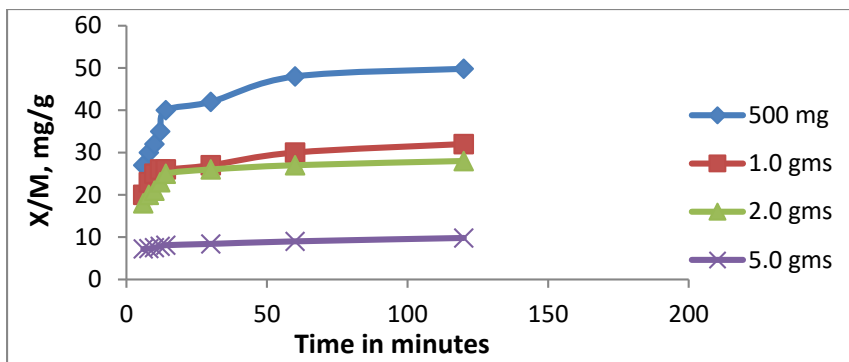


Fig.3- Plot of adsorption capacity vs. time for Hg²⁺ by Stalks of Prunuscercasus

Effect of pH:

pH of the solution influences electrostatic binding of the ions to the corresponding sites. It also influences the site dissociation and also the solution chemistry of the heavy metals such as hydrolysis, binding by organic and inorganic ligands, redox reactions. The extent of functional groups on the sorbent and the nature of the cationic species are also affected by changes in the pH of the solution. Adsorption pattern on **Stalks of Prunuscercasus** is slightly different; a continuous increase is seen in % adsorption with rise in pH. For pH 5, 6 and 7 the % adsorption is 50.5, 63.5 and 65.4 respectively. (Fig-4) At low pH protons would compete with metal ions for the active sites responsible for the biosorption and decrease the metal sorption. At pH less than 2.0 all the binding sites may be protonated and thereby even desorbs all metal bound to the biomass. As pH increases the concentration of protons decreases, allowing more metal to be adsorbed. As a general rule the acidic dissociation constant of an aquometal ion is greater, greater is its oxidation state. The hydroxide/ hydrous oxides of metal in +2 oxidation state have a tendency to undergo hydrolysis beyond pH 6, (Fig-4)

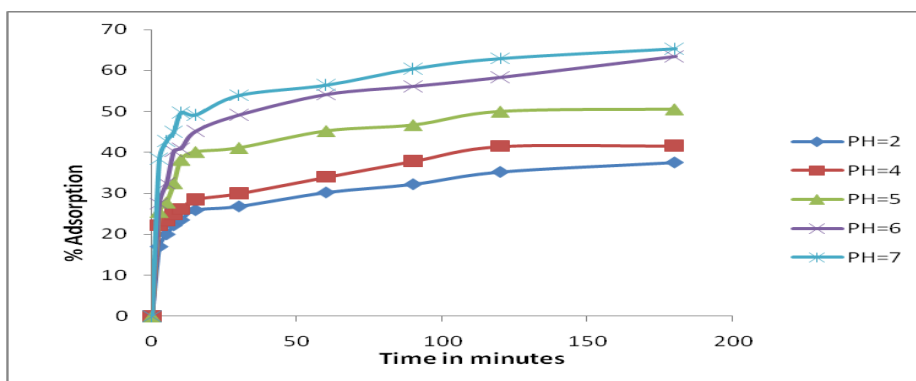


Fig-4 Effect of pH on % adsorption of Hg²⁺ by stalks of prunuscercasus

Effect of temperature:

The study of adsorption of Hg²⁺ under optimum conditions, revealed that with increase in temperature there is a substantial increase in % adsorption by **stalks of prunuscercasus** also shows an increasing trend in adsorption with rise in temperature. **stalks of prunuscercasus** show

enhancement in adsorption from 37% at 15 °C to 65 % at 45°C. Fig-5, as the temperature is increased from 15 °C to 45°C. These results indicate that the process of adsorption of the metal ion on stalks of prunuscerasus is endothermic in nature. In addition to the endothermic nature of the process, another reason for this enhancement in uptake could be an increase in the pore size with rise in the temperature, similar enhanced ion exchange capacity with rice as biosorbent is also reported in literature. This could also be due to the centers developed on the surface by treatment of the raw material with sulphuric and nitric acid during preparation. The optimum temperature for working with stalks of prunuscerasus appears to be at 45°C.

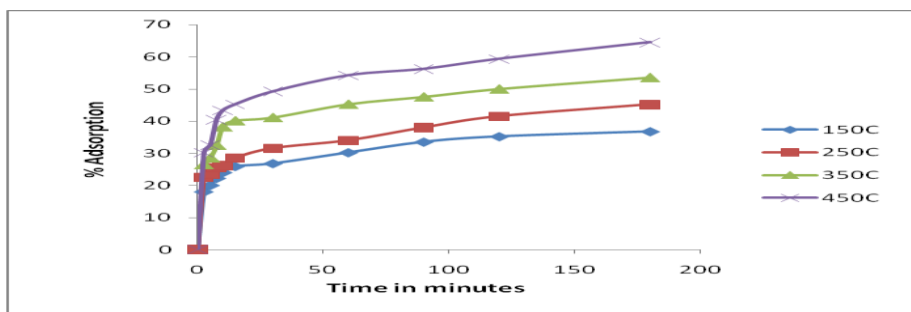


Fig-5 Effect of temperature on % adsorption of Hg₂⁺ by 2.0 gm, stalks of prunuscerasus

Thermodynamic studies of adsorption of Hg₂⁺

The equilibrium constant KD for adsorption on stalks of prunuscerasus were calculated from the experimental data. From the values of KD at different temperature it can be concluded that adsorption is an endothermic and temperature activated process. The ΔG values on stalks of prunuscerasus, are +ve at 15 °C, 25 °C, and 35 °C with the values decreasing with increasing temperature. At 45 °C ΔG = - 1013 j/mol (Table-2). This indicates that the adsorption on stalks of prunuscerasus is a highly energy activated process. The isosteric heat of adsorption for Hg₂⁺ ions on stalks of prunuscerasus was calculated using the formula.

$$\Delta H_{\text{adsorption}} = \frac{R \ln C_2 / C_1}{1/T_1 - 1/T_2}$$

The value of ΔH adsorption was found to lie between 8.16 kJ/mole. to 3.022 kJ/ mole over the temperature range studied. An increase in the value of KD from 0.5225 to 2.264(Table-2) with rise in temperature indicates that at higher temperature the mobility of the Hg₂⁺ ions is enhanced resulting in the effective interaction between the sorbent and sorbate.

Table-2

Temperature in K	KD	ΔG J/mole
288	0.5225	+1485.4

298	0.9945	+860.14
308	2.264	+10.24
318	2.264	-1013

Adsorption isotherms

To explain the adsorption of Hg²⁺ on **stalks of prunuscerasus**, the data obtained from the adsorption experiments was fitted in to Langmuir and Freundlich adsorption isotherm models. The applicability of the models was checked by plotting graphs of Ce/qe vs. Ce and log Ce vs. log x/m respectively. The plots of Ce/qe vs. Ce for adsorption on sorbent stalks of prunuscerasus were straight lines however the values of Langmuir constant were negative indicating the no applicability of this model. The Freundlich equation gave plots with **stalks of prunuscerasus** shows K= 46.2 and 1/n = 1.124, R²= 0.933. From this data one can conclude with caution that the sorption of Hg²⁺ ions cannot be explained completely by this model. The adsorption of metal cations on the modified surface of stalks of Stalks of Prunuscerasus appears to be governed not by any single mechanism but by different mechanisms such as ion-exchange, complexation etc.in addition to adsorption.

Kinetic studies:

Kinetics of adsorption of Hg²⁺ ions on **stalks of prunuscerasus** was modeled by the pseudo first order equation proposed by Lagergren. The plots of log (qe-qt) vs. t yielded plots as shown in fig.6, using various sorbent doses. For the sorbent **stalks of prunuscerasus** the plots of log (qe-qt) vs. t are expected to yield straight lines if adsorption follows pseudo first order reaction. The data was also fitted in the pseudo second order model proposed by Ho and McKay. The plots of t/qt vs. t yielded straight lines as shown in Fig-6 with linear regression coefficient of 0.99 (Table-3) and second order rate constant K₂ = 0.699.(Table-3) It can thus be concluded that the adsorption of Hg²⁺ on stalks of prunuscerasus obeys the second order kinetics.

Table-3

Adsorbent	K ₂	R ²
stalks of prunuscerasus	0.699	0.99

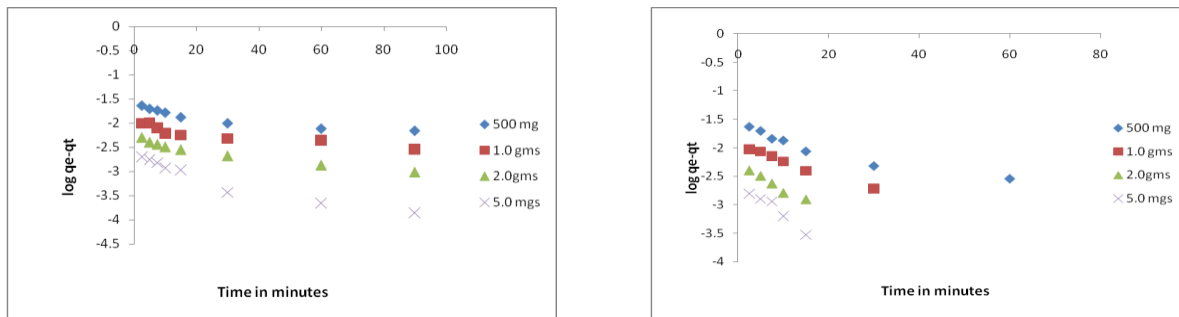


Fig. 6 Plot of (log qe-qt) vs. Time for adsorption of Hg²⁺ ions by stalks of prunuscerasus

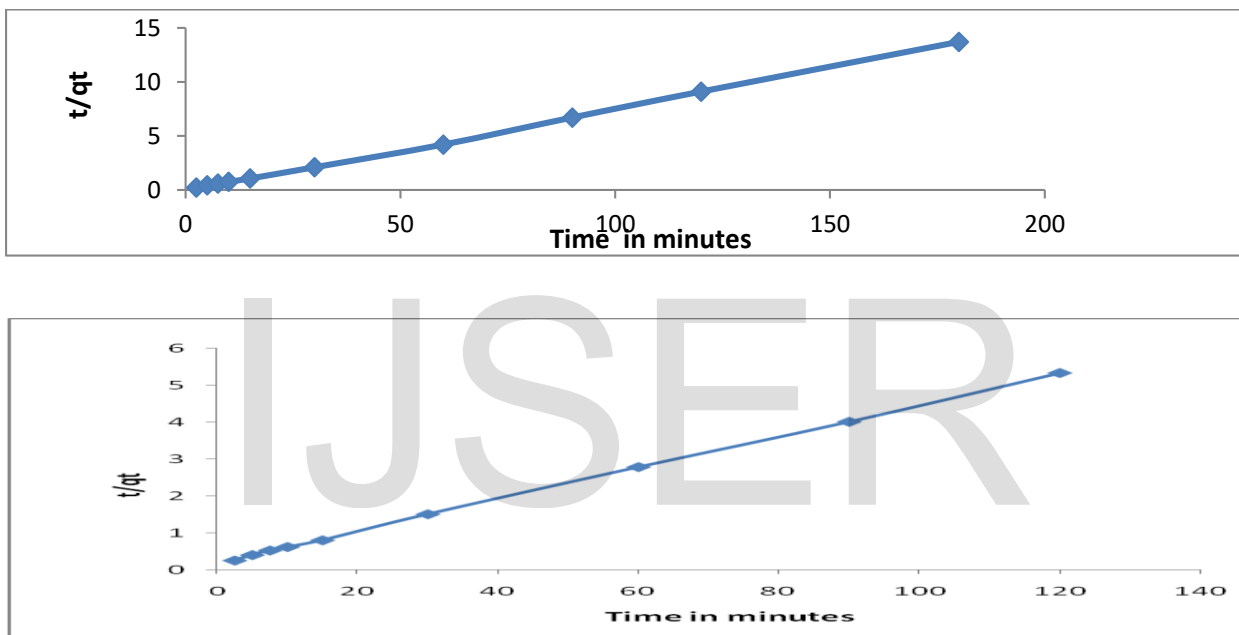


Fig.7 Plots of t/qt vs. Time for adsorption of Hg²⁺ ions by stalks of prunuscerasus

Webber –Morris intraparticle diffusion model:

Adsorption kinetics is usually controlled by different mechanisms, the most limiting mechanism being the diffusion mechanism. The plots of Q vs. t^{1/2} show three portions. The initial curve portion is attributable to rapid external diffusion or boundary layer diffusion. The plot in Fig.8 indicates that the major contribution to adsorption can be attributed to intraparticle diffusion .For all material doses studied the contribution of boundary layer diffusion is insignificant.

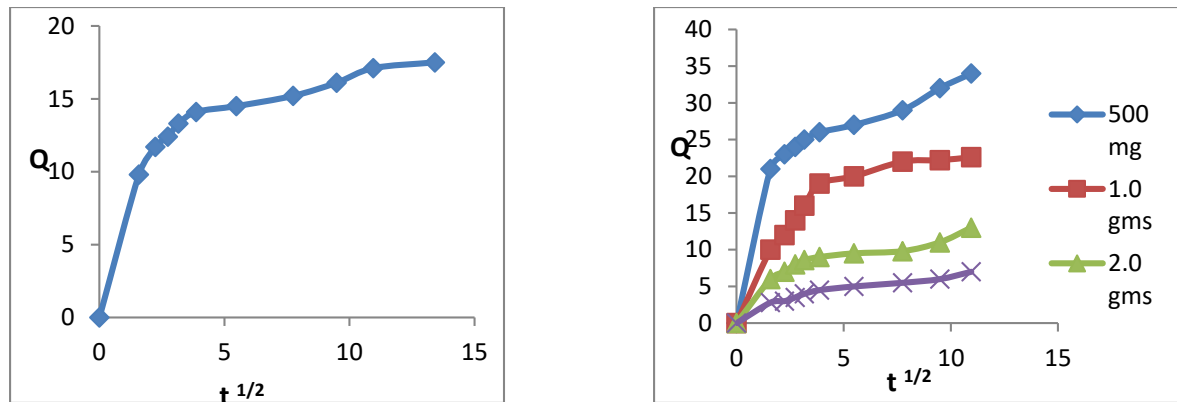


Fig.8 plot of Q vs $t^{1/2}$ for stalks of prunuscerasus

CONCLUSIONS

Biosorption of Hg^{2+} ions by Sulphonated biomass stalks of prunuscerasus is conducted in batch conditions. The effect of different parameters such as contact time, sorbent dose, pH and temperature has been studied. Adsorption kinetic modeling data were found out. The kinetics of biosorption results shows that sorption process is well explained by pseudo-second order model with determination coefficients higher than 0.94 for sorbent under all experimental conditions. A 5 gm dose of shows maximum adsorption is about 65%. Optimum pH for adsorption of mercury, stalks of prunuscerasus pH 7 is better. The % adsorption decreases from 65% (pH=7). The adsorption follows the Freundlich model with K_f values of 45.11 and 46.2 for stalks of prunuscerasus, indicating good adsorption. Kinetic modeling indicates that the adsorption follows pseudo second order kinetics. K_2 values for stalks of prunuscerasus is 0.699, with R^2 0.99. The value K_p is found to be 0.60 to 2.50 for initial and final concentrations. Thermodynamic parameter via KD , ΔG has also been calculated to determine the spontaneity of the process. The low value of activation energy indicates that sorption is an activated and physical process. Thus sulphonated biomass of Stalks of Prunuscerasus a low cost and easily available efficiently used as an excellent sorbent for the removal of Hg^{2+} from wastewater. The results of adsorption studies of Hg^{2+} on stalks of prunuscerasus. In this ways, the current processed adsorbents acts better material than other reported materials.

Because the result obtained for this material shows Equilibrium time for adsorption of Hg^{2+} by stalks of prunuscerasus is 120 minutes. A 5 gm dose of shows maximum adsorption is about 65%. Optimum pH for adsorption of mercury, stalks of prunuscerasus pH 7 is better for this adsorbent compared to other sorbent. The % adsorption decreases from 65% (pH=7) ΔG values for adsorption on stalks of prunuscerasus are positive for 15°C, 25°C, 35°C, while ΔG value at 45°C is negative. Increase in KD values is observed on stalks of prunuscerasus from 15°C -45°C The adsorption follows the Freundlich model with K_f values of 45.11 and 46.2 for stalks of prunuscerasus, indicating good adsorption. However the possibility of other mechanisms such as ion exchange complexation cannot be ruled out particularly on stalks of prunuscerasus, as the values of coefficient of determination is 0.933. Kinetic modeling indicates that the adsorption follows pseudo second order kinetics. K_2 values for stalks of prunuscerasus is 0.699, with R^2

0.99. The current results obtained with the sulphonated biosorbent are found to be comparatively good since, the material is easily available. low cost and shows ecofriendly adsorption as compared to the other forms of biosorbents of Cicer areintinum like Sulponated, phosphated etc. for the removal of Hg^{2+} , Hg^{2+} , Cu^{2+} heavy metals ions from waste water.

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