

Biosorption of Mercury onto Protonated Pistachio Hull Wastes – Effect of Variables and Kinetic Experiments

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Abstract—Batch parametric experiments were performed to study the applicability of protonated pistachio hull waste as a sorbent with respect to the effect of pH of the solution, initial metal concentration, sorbent dosage and temperature on the metal removal efficiency. Optimum conditions for mercury removal were found to be pH 7.0 and adsorbent dose - 1.0 g/L. The metal uptake increased with increase in the initial concentration of the metal. The sorption process was identified as endothermic in nature favouring use of high temperature. The kinetic studies revealed that pseudo-second order model fitted well and the constants were determined. The pseudo-second order rate constant and maximum uptake capacity were found as $1.99 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ and 48.78 mg g^{-1} with 50 mg L^{-1} metal concentration. Thermodynamic studies were conducted and the activation energy for the adsorption of mercury onto was found to be 10.26 KJ/ mol .

Index Terms—Absorbent, metal removal, pistachio hull waste.

I. INTRODUCTION

Rapid development of metal plating industries, mining activities, tanneries, fertiliser and paper industries has led to the direct or indirect release of heavy metals into the environment. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment [1]. The harmful heavy metals of immediate priority are identified as nickel, mercury, copper and zinc. Mercury is reported to be a neurotoxin and can cause irreparable damage to the central nervous system. High mercury dosages can cause impairment of pulmonary and kidney function, chest pain and dyspnoea [2]. Faced with stringent regulations, treatment of heavy metal treatment is of utmost importance. Numerous methods are practised in order to treat the metal contaminated effluent such as precipitation, ion exchange, electrolysis, separation by membrane, adsorption, etc. The method of wastewater treatment is selected according to the concentration of the waste and the cost of treatment [3]-[5].

Adsorption is one of the more popular methods for the removal of metals ions from the aqueous solutions. Adsorption is a physical phenomenon where no chemical reaction takes place. It is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent [6]. Activated carbons, because of their high surface area, micro porous character and the chemical nature of surface,

have been a popular adsorbent for the removal of heavy metals from aqueous solutions. Due to high cost and losses of activated carbon in the application processes, there is growing interest in using low-cost alternative materials including clays, zeolites, coal, fly ash, peat, siderite, agricultural waste, charcoal. Agricultural wastes and industrial by products offer a good choice and has many advantages like simple technique; requires little processing; good adsorption capacity; selective adsorption of heavy metals; low cost; free availability and easy regeneration [7]. Studies on the efficiency of sawdust in the removal of Cu^{2+} and Zn^{2+} ions were conducted [8]. Removal of copper by dehydrated wheat bran has been reported [9]. Many studies have been conducted on the potential of industrial by-products for metal removal, such as red mud, calcined phosphate and clarified sludge. Biosorption is being demonstrated as a useful alternative to conventional systems for the removal of toxic metals from industrial effluents. Adsorption of copper, zinc, lead and cadmium onto the carbon produced from nutshells of walnut, hazelnut, pistachio, almond, and apricot stone has been investigated [10]. In this background, this research study is aimed at utilisation of protonated pistachio hull waste as an alternative biosorbent for the removal of mercury from its aqueous solution. Effect of process variables like pH, biosorbent dose, initial metal concentration and temperature on the metal remove efficiency was studied. The mechanism of sorption was investigated through kinetic experiments. Thermodynamic studies were performed to estimate the activation energy.

II. MATERIALS AND METHODS

A. Pistachio Hulls Waste-Sorbent Preparation

Pistachio Hulls Waste (PHW) were obtained from nuts market. The hulls were washed using the tap water followed by distilled water in order to remove the impurities. Hull waste was dried in sunny ambient air for 3 days and subsequently crushed in order to reduce the size of the particles. The reduced size was ground using a high speed grinder and sieved, where the final size of PHW between $0.063\text{-}0.106 \text{ mm}$. Finely powdered adsorbent is acid activated by soaking the PHW in 0.1 M HCl for 24 hours in order to protonate the surface and was dried at 35°C overnight. A weight loss of approximately 11% was observed. The acid activated adsorbent is termed as “Protonated Pistachio Hull Waste (PPHW)”.

B. Parametric Studies

The stock solutions (1000 mg/L) of Hg^{2+} was prepared by dissolving $\text{Hg}(\text{NO}_3)_2 \cdot 1/2 \text{ H}_2\text{O}$ in double distilled water and

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stored in refrigerator. To study the effect of parameters such as adsorbent dosage, pH, initial concentration and the temperature for the removal of metal, batch experiments were carried out in a temperature controlled shaker at room temperature. The adsorption isotherm experiment was carried out by agitating 100mL metal solutions of various concentrations. After agitation, the mercury solutions were separated from the adsorbent by filtration using Whatmann no.4 filter paper. Metal concentration in the supernatant solutions was measured using an atomic absorption spectrophotometer. The effect of initial pH on metal removal was studied over a pH range of (2.0–9.0). The initial pH of the metal solution was adjusted by the addition of 0.5M solution of H₂SO₄ or NaOH. To find the optimum amount of adsorbent per unit mass of the adsorbate, the metal solution (100 mL) was contacted with different amounts of PPHW till equilibrium was reached. The sorbent dosages were studied in range 1.0–7.0 g/L. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms at 303, 313, and 323 K with a fixed metal concentration and dosage. The metal removal percentage and uptake were calculated using the following relationships:

$$\% \text{ Removal efficiency (RE \%)} = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (1)$$

$$\text{Metal uptake, } q_e = \frac{[(C_0 - C_e) \times V]}{m} \quad (2)$$

C. Kinetic Studies

The kinetic studies were conducted to estimate the contact time required for the attainment of equilibrium between the dissolved and solid bound adsorbate. This set of experiments were carried out by agitating with 100mL of metal solutions whose concentrations were 50, 100, 150 and 200mg /L at the optimum pH with 1.0 g/ L of PPHW in a shaker operated at room temperature. In order to identify the adsorption mechanism, the rate constants for chemisorption and intra-particle diffusion for mercury were determined using the models for pseudo-second-order [11] and intra-particle diffusion model [12]. The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_1^2} + \frac{1}{q_1} t \quad (3)$$

where q_1 (mg/ g) is the maximum adsorption capacity and q_t (mg/ g) is the amount of metal adsorbed at time, t , and k_2 (g/ (mg min)) is the equilibrium rate constant for pseudo-second order adsorption.

The intra-particle diffusion kinetic model is expressed as:

$$q_t = k_t t^{1/2} + C \quad (4)$$

where k_t (mg / (g min^{1/2})) is the intra-particle diffusion rate constant and C (mg/ g) is a constant that is related to boundary layer thickness.

D. Determination of Activation Energy

The thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. Arrhenius equation Eq. (5) represents the effect of temperature on rate

constant and is represented as:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (5)$$

where k is the rate constant obtained with the best fit kinetic model (at different temperatures), E_a , (kJ/mol) is the activation energy, A (g/(mg min)), is the Arrhenius factor, R , is the gas constant and $T(K)$ is the solution temperature.

III. RESULTS AND DISCUSSION

A. Effect of pH

Metal speciation is a vital phenomenon occurring during the adsorption of metal on sorbent surface. pH is reported to be influencing metal speciation and dissociation of active functional sites on the sorbent. The effect of pH on the adsorption of Hg by PPHW was studied by varying the pH of the metal solution from 3.0 to 9.0 under constant experimental conditions (initial metal concentration = 100 mg/L, sorbent dosage=1 g/L, a contact time 90 min and temperature 30 °C). Fig. 1 shows the dependence of removal efficiency of free ionic Hg on pH. It can be observed from the figure that the removal of Hg (II) increases with increase in pH from 28 to 92% over pH range from 3.0 to 9.0. This increase in pH may be due to the presence of negative charge on the surface of the adsorbent that may be responsible for metal binding [13]. Decreased removal efficiencies at lower pH is due to the hydrogen ions competition with the metal ions for the sorption sites in the sorbent. This behaviour can also be related to the pH_{Zpc} value of PPHW which was estimated as 4.8 according to procedure given [14]. When the solution pH is less than pH_{Zpc}, the surface is positively charged and the sorption of cationic metal will be less. But, when the pH is more than pH_{Zpc}, the surface charges become more negative favouring better interaction with the metal [10]. The optimal pH was found to be 7.0. Similar observations were reported on the studies on removal of Cu on PHW [13].

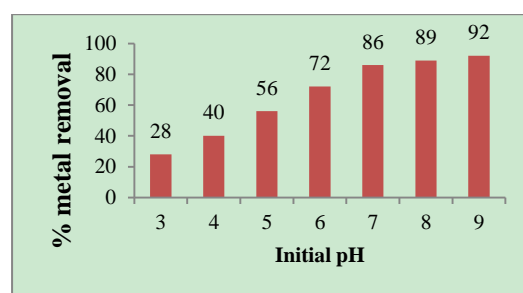


Fig. 1. Effect of initial pH of the solution on the sorption of Mercury by PPHW ($t=90$ min; $C_0=100$ mg/L, $M=1.0$ g/L and $T=30$ °C).

B. Effect of Sorbent Dose

The effect of sorbent dose on the adsorption of Hg (II) by PPHW was studied with the range of the adsorbent from 1.0 to 7.0 g/L with initial metal concentration of 100 mg/L and optimal pH 7.0. The percentage removal of Hg (II) versus adsorbent dosage was shown in Fig. 2. It can be observed from the figure that the removal of Hg (II) increase with increase the dosage from 10 to 94% over dosage range 0.1 to 0.7g. This finding shows that 7.0 g/L of adsorbent has enough

exchangeable sites to remove the ions [13]. The phenomenon of increasing removal of Hg (II) with increase in adsorbent dose may be explained as with increase in adsorbent dose, more and more surface area become available for metal ion to adsorb and this increased the removal efficiency [15]. But the adsorbent dosage was found to have negative effect on Hg (II) uptake, which decreases with increase in sorbent dosage in the same range. It was observed that the uptake of Hg (II) decreased with the increase in the adsorbent dosage as shown in Fig. 3. Similar observations were reported in other studies [13], [16], [17].

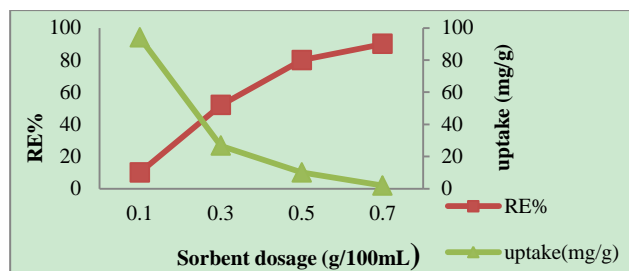


Fig. 2. Effect of sorbent dosage on percentage removal and metal uptake for the sorption of Mercury by PPHW ($t=90\text{min}$, $C_0=100\text{ mg/L}$, $\text{pH}=7$ and $T=30\text{ }^\circ\text{C}$).

C. Effect of Initial Metal Concentration

The influence of Hg^{+2} concentrations on the sorption by the AAPHW was investigated by varying the Hg^{+2} concentrations from 50 to 200 mg/L at pH 7.0 for 90 min equilibrium time. From the Fig. 3, it was evident that the metal uptake increased with the increase in C_0 . Overall, the rate of Mercury uptake was higher with in first 30 min contact time [18]. But, the removal percentages decreased with increase in metal concentrations. The increase of initial Hg^{+2} concentrations resulted in a reduction of its adsorption percentage due to limited adsorption sites ratio of metal to PPHW [16].

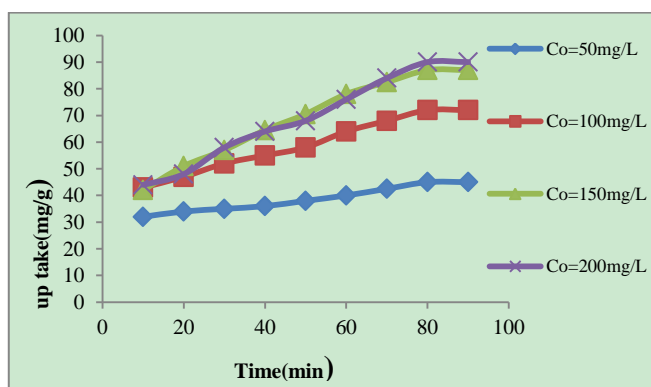


Fig. 3. Effect of initial metal concentration on uptake ($t=90\text{min}$; $M=1.0\text{g/L}$, $\text{pH}=7$, $T=30\text{ }^\circ\text{C}$).

D. Effect of Temperature

The effect of temperature on the removal of mercury was studied in the range of 303-323 K at optimal pH 7, initial metal concentration 100 mg/L and sorbent dosage 1.0 g/L. The equilibrium sorption capacity of mercury increased with increase in temperature and was shown in Fig. 4. Thus, the sorption process was identified as endothermic in nature [10]. Since adsorbent is porous and possibilities of diffusion

adsorbate cannot be ruled out, increase in the sorption with the rise of temperature may be diffusion controlled which is endothermic process [13]-[15]. Other researcher [10] also observed similar temperature effects on metal sorption studies. But, the magnitude of the effect was found to be different among these studies.

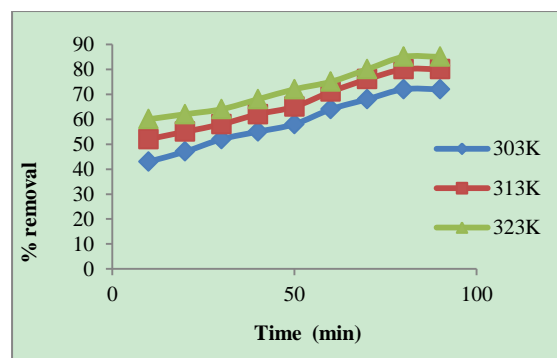


Fig. 4. Effect of temperature on metal removal for the sorption of mercury by AAPHW ($t = 90\text{min}$, $\text{pH}=7$, $C_0=100\text{ mg /L}$ and $M=1\text{g/L}$).

TABLE I: KINETIC MODEL CONSTANTS

Kinetic model	Initial metal concentration(mg/L)			
	50	100	150	200
Pseudo second order				
$k_2(\text{g mg}^{-1} \text{min}^{-1}) \times 10^3$	1.99	0.77	0.412	0.34
$q_1(\text{mg g}^{-1})$	48.78	82.64	107.5	113.64
R^2	0.976	0.992	0.989	0.99
Intraparticle diffusion				
$k_i(\text{mg g min}^{-1/2})$	2.2	4.9	7.67	8.4
C	23.07	25.19	29.67	31.73
R^2	0.944	0.978	0.969	0.976

E. Kinetic Studies

The transient behaviour of the metal adsorption process was studied through kinetic experiments and analysed using pseudo-second-order and intra-particle diffusion model. The values of k_2 at different initial metal concentrations for all adsorbents were calculated from the slopes of the respective linear plots of t/q_t vs. t . Fig. 5 show Pseudo-second-order kinetic plots for the sorption of Mercury on PPHW at 303, 313 and 323K. The fitness of experimental data to pseudo-second order model implies that adsorption is likely controlled by chemisorptions, including the sharing or exchanging of electrons between metal ion and adsorbent [10], [19]. The correlation coefficient was found to be > 0.97 , suggesting a strong relationship between the parameters and also explains that the process follows pseudo-second-order kinetics. A plot of q_t vs. $t^{1/2}$ was made to test the intra-particle diffusion as shown in Fig. 6; if it passes through origin, intra-particle diffusion is the only rate controlling step [20]. This possibility was tested in terms of a graphical relationship between the amount of metal adsorbed and square root of time at different initial metal concentration. All the plots have the same general aspect. They all have an initial curved portion, followed by an intermediate linear portion. The initial portion of these plots is related to mass transfer and the linear part is due to intra-particle diffusion. Previous studies showed the same features of the plots of q_t

vs. $t^{1/2}$ which characterize the different steps of adsorption process [19], [21]. The values of rate constant for intra-particle diffusion, (k_t) at different initial metal concentration for all adsorbents was determined from the slopes of the linear portions of the respective plots and were given in Table I. The results revealed that the R^2 was greater for pseudo second order model compared to the other.

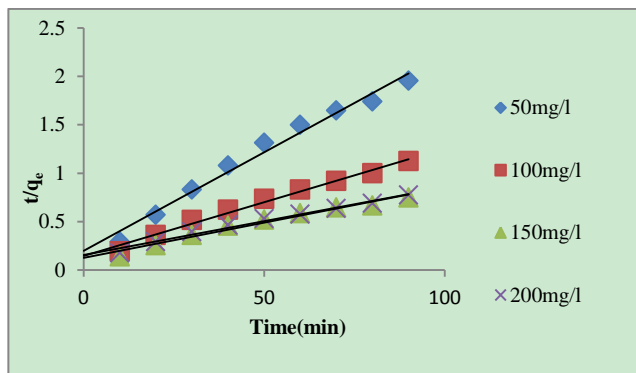


Fig. 5. Pseudo-second-order model for the sorption of Mercury on PPHW.

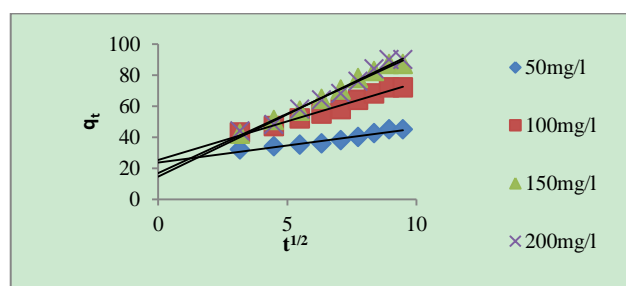


Fig. 6. Intra particle diffusion model for the sorption of Mercury on PPHW.

F. Thermodynamic Studies

The thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. The rate constant from the best fit model, pseudo-second-order kinetic model. K_2 was chosen to plot of $\ln k_2$ versus $1/T$ and shown in Fig. 7. The slope of the best fit line revealed the Activation energy (E_a) of the biosorption process to be 10.26 KJ/ mol with PPHW. This fact is consistent with the properties of the adsorbent and Langmuir-type adsorption isotherm.

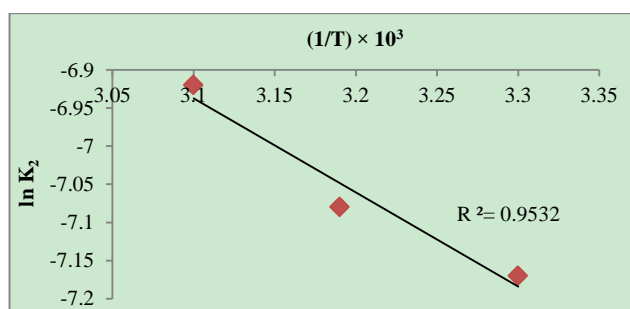


Fig. 7. Arrhenius plot.

IV. CONCLUSIONS

Protonated pistachio hull waste has been proved as a potential sorbent for the removal of mercury from its aqueous solution. Effect of operating parameters, such as pH, sorbent dosage, initial metal concentration and temperature, on the metal removal efficiency were studied. The optimal pH was

found to be 7.0 and adsorbent dose was found to be 1.0 g/L. The sorption process was identified as endothermic in nature. Two different kinetics models (pseudo-second-order and intra-particle diffusion) were studied to analyse the transient behaviour of the metal adsorption process. Pseudo-second-order model was the best model representing the adsorption of Hg^{+2} . From thermodynamic studies, activation energy for the adsorption of was found to be 10.26 kJ/ mol.

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