Technical paper

Utilisation of Flame Tree Waste Biomass for the Removal of Hg(II) from Water

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Abstract

Activated carbon prepared from sulphuric acid treated Flame tree pods' has been used for the removal of Hg(II) from aqueous solution. Batch mode experiments were conducted to assess the potential for the removal of Hg(II) from water using the above carbon. Adsorption experiments showed that the adsorption process follows the pseudo second order kinetic model and the equilibrium data were fitted well with both Freundlich and Redlich–Peterson isotherm model. About 92% of mercury (II) adsorbed was recovered from the spent carbon using distilled water (pH: 1) and 3% KI solution.

Keywords: Flame tree pods, Freundlich model, Redlich–Peterson model, pseudo second order, desorption

1. Introduction

The presence of heavy metals over permissible levels in drinking water may cause adverse effect on human physiology. Mercury ion is one of the most toxic pollutants introduced into natural water mainly from the discharge of the chlorine manufacturing industry, paper and pulp, plastic and battery manufacturing industries. The tolerance limit for Hg(II) for discharge into land surface water is 10.0 μg/L and for drinking water 1.0 μg /L.[1] Mercury (II) mainly damages the central nervous system and kidney.[2] The harmful effects of methyl mercury include the contamination of fish in Minamata bay near Japan.[3] Many treatment processes for the removal of mercury (II) from wastewater have been reported in the literature, mainly chemical precipitation, reverse osmosis, membrane filtration, ion exchange and adsorption. The most commonly used method is adsorption using activated carbon. Adsorption of Hg(II) studied by using various types of low cost adsorbents has been reported in the literature. Many reports are there on the development of activated carbon from readily available materials. In this work, we used Flame tree pods' (*Delonix regia*) a member of bean family which produces brown woody seed pods that lengths upto 60 cm as a raw material to derive activated carbon. The main objective of the work is to investigate kinetic and equilibrium parameters of this adsorbent for the removal of Hg(II) from aqueous solutions.

2. Materials and Methods

2. 1. Preparation of the Adsorbent

The pods' of *Delonix regia* collected from NIT campus, Tiruchirappalli (India) was dried and cut into small pieces. The small pieces were treated with concentrated sulphuric acid (36N) at 1:1 (W/V) ratio for 48 hours and activated at 160 °C for 6 hours in an air oven. The resulting carbon was washed with distilled water several times till the pH of the wash water becomes the pH of the distilled water and dried at 105 ± 5 °C in an oven. The carbon obtained from Flame tree pods' was designated as FTPC. The carbon was ground to powder and the portion retained between 0.104–0.178 mm sieves were used for the study. All the chemicals used are of analytical grade.

2. 2. Characterisation of the Adsorbent

The pH of the carbon was found to be 4.1 due to the existence of the functional groups like phenol, carboxylic acid and sulphuric acid groups. The various functional groups present on the surface of the carbon is confirmed through the IR spectrum. The IR spectrum of the prepared activated carbon was recorded in the range of 4000 to 450 cm^{-1} using KBr disk as reference. The BET surface analyzer was used to find out the surface area and the micropore area (6.7689 m^2/g) of the carbon. The Scanning Electron

Microscope was used to study the surface morphology of the plain FTPC and Hg(II) loaded FTPC. The SEM picture is given in Figure 1. The physico-chemical characteristics obtained for FTPC are summarized in Table 1.

Table 1. Characterization of FTPC.

Parameter	FTPC
pH	4.10
Moisture content (%)	8.0
Bulk density (g/cc)	0.663
Ash content (%)	3.0
Water soluble matter (%)	1.1
Acid soluble matter (%)	4.2
Decolourising power (mg/g)	138
Ion exchange capacity (meq./g)	0.6
Surface area (m^2/g)	4.08
Ash analysis (%)	
Na_2O	NDQ
K_2O	NDQ
Fe (mg/L)	0.99

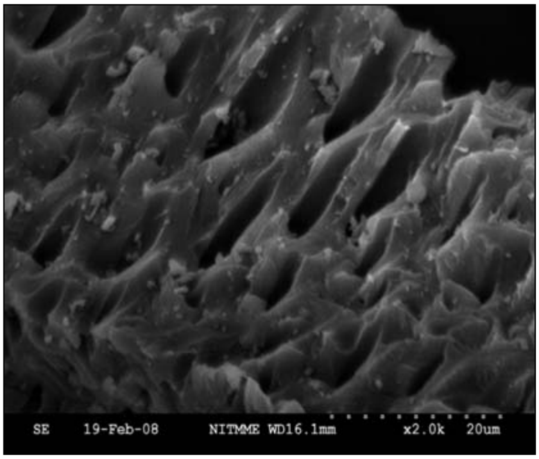

Figure 1: SEM picture of plain FTPC.

2. 3. Batch Mode Studies

A stock solution of 1000 mg/L of Hg(II) was prepared by dissolving 0.3385g of $HgCl_2$ in 250 mL of distilled water. Solutions of desired concentration were prepared by diluting the stock solution using distilled water. The required pH of the Hg(II) solution was adjusted by using various concentrations of dil.HCl (0.001, 0.01&0.1 M) and dil.NaOH (0.001, 0.01&0.1 M).Batch mode experiments were conducted using screw capped closed containers and Orbitek shaker at 300 rpm. A calibration graph of absorbance versus concentration of Hg(II) was obtained using systronics photometer (model 104) at λ_{max} 575nm. The residual Hg(II) ion concentration was estimated by Hg(II) as the ternary complex with Rhodamine 6G and Iodide.[4] For pH study 100 mL of 20 mg/L solutions were adjusted to different pH (2.0–10.0) and shaken with 20 mg of FTPC for 5 hours. The influence of carbon dose was done by agitating 100 mL of 40 mg/L of Hg(II) solutions with different amounts of carbon dose (10–100 mg) after adjusting the pH = 5±0.1 for 5h. The effect of contact time was carried out by shaking two different concentrations of Hg(II) solutions (5,10 mg/L) with 20 mg of carbon dose in 100 mL of solution after adjusting the pH of the solution to 5±0.1 for predetermined periods of time. For isotherm studies 30 mg of FTPC and 100 mL of different initial concentrations (10 to 100 mg/L) of Hg(II) solution having pH = 5±0.1 were taken and shaken for 5h. Desorption study was also carried out by using 20 mg/L of Hg(II) solution with 20 mg of FTPC. The spent carbon was agitated with distilled water having different pH (1–6 using dil.HCl) values and different concentration of KI solution at 30 °C. The graphical representations were performed using Solver Excel spread sheet and Origin 6.0 software packages.

3. Results and Discussion

3. 1. Effect of Carbon Dose

Figure 2 shows the removal of Hg(II) as a function of carbon dosage. Removal of Hg(II) increased from 53% to 98.6% with the increase of dose from 5 mg to 100 mg. This is mainly due to the increasing number of active sites for more adsorption of ions. A minimum amount of 50 mg of FTPC was required for 95% of Hg(II) removal from 40 mg/L solution.

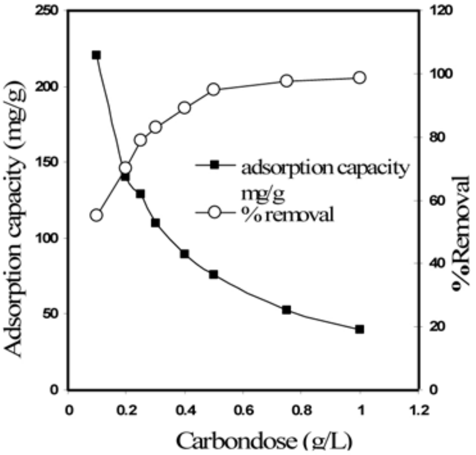

Figure 2: Effect of carbon dose.

3. 2. Effect of pH and Mechanism of Adsorption

Figure 3 shows the effect of influence of initial pH on the removal of Hg(II) by FTPC. This study partly explains the mechanism involved in the removal of Hg(II) by FTPC. The removal was effective over the pH range 4.0–10.0. But at higher pH values (after 6) the predominant species was $Hg(OH)_2$. Kurbatov[5] first recognized the pH dependence of adsorption in 1951. Since then it has become progressively recognized that pH is the master variable that governs the extent of adsorption.[6] At low pH there is very low adsorption, and increase of pH leads to increase of adsorption from 40 to 99.8%.

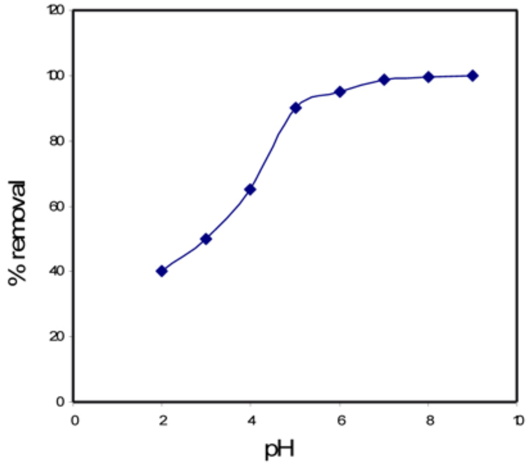

Figure 3. Effect of pH on the removal of Hg(II)

At high pH values, the curve rises steeply to reach a plateau. This is explained by the following reasons.

1. A rapid increase in uptake of the metal ion usually occurs over a narrow pH range. This is particularly true for the strongly hydrolysable cations[7] and this uptake is due to an ion exchange reaction between H^+ and Hg^{2+} ions. There is a decrease in the pH of the Hg(II) solution after the removal of Hg(II) from the solution by FTPC. This shows there is proton release from the surface of the carbon due to cation exchange between the H^+ ion from the carbon surface and the metal ion from the solution.[8] This reveals that the increase in the pH of the solution deprotonate the acidic groups on the surface of the carbon and provides more negative sites for the sorption of Hg(II) ions from solution.[9] Whereas at low pH, there would be more number of hydrogen ions in the solution that prevents the negative charge formation on the carbon surface and reduces the uptake of the metal. The initial adsorption of metal ion on the carbon surface is mainly due to ion exchange mechanism[10] and is reported in the case of adsorption of cationic form of dyes also on the carbon surface.[11]
2. The ratio of H^+/ Hg^{2+} ion exchange adsorption is frequently less than one. Sometimes the adsorbed species may not be Hg^{2+}, but a lower charged ion pair or hydroxo complex ion. The effect of complex formation on overall adsorption of a metal ion will depend on the stability of the complex formed and the relative affinity of the surface for the free and complexed forms of metal.[12,13] If the stability of the cation-carbon surface is large compared with the stability of the cation complex-carbon in solution, then the complex formation in solution will have very little effect on the overall extent of adsorption.

3. 3. Sorption Isotherm Models

Adsorption isotherm is the relationship between the adsorbate in the liquid phase and the adsorbate adsorbed on the surface of the adsorbent at equilibrium at constant temperature. The equilibrium adsorption isotherm is very important to design the adsorption systems. For solid-liquid systems, several isotherm equations are available. The Langmuir isotherm[14] takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent, the equation is

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{1}$$

The Freundlich isotherm[15] is an empirical equation employed to describe the heterogeneous system. The equation is given below:

$$q_e = K_F C_e^{\,1/n} \tag{2}$$

The Redlich-Peterson isotherm[16] combines both Langmuir isotherm and Freundlich isotherm equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. The equation is

$$q_e = \frac{A C_e}{1 + B C_e^{\,g}} \tag{3}$$

In the above equation, constant g is the exponent, which lies between 0 and 1. If constant g is equal to one, the equation modifies to Langmuir model, if constant g is equal to zero then the equation changes to Henry's law equation.

The fitted isotherms are shown in Figure 4. The maximum of adsorption of Hg(II) on FTPC was found to be 135.4 mg/g. The χ^2 value of Freundlich isotherm (0.201) is very low compared to Langmuir isotherm (20.2). The χ^2 value of Redlich-Peterson (0.28) is very close to Freundlich isotherm. This is clearly shown is Figure 5.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor $K_{R.}$

$$K_R = \frac{1}{(1 + K_L C_0)} \tag{4}$$

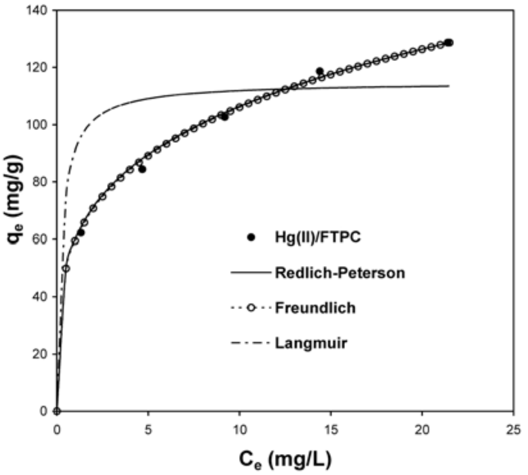

Figure 4: Fitted Isotherm models for Hg(II) adsorption on FTPC.

The value of $K_{R,}$[17,18] explains the feasibility of the reaction ($K_R > 1$ – unfavourable, $K_R = 1$ – linear, $0 < K_R < 1$ – favourable, $K_R = 0$ – Irreversible) K_R value obtained (0.1175– 0.0425) between 0 and 1 indicates favourable isotherms for Hg(II)-FTPC system. The K_R value decreases with increase in the number of metal ions in solution and the increase of pH also lowers the value due to the increase of more negative sites on FTPC. This leads to the electrostatic attraction between the metal ions and the negative sites on the surface of the carbon. The fitted isotherm parameter values are given in Table 2.

Table 2: Parameters for the fitted isotherm models for the FTPC-Hg(II) system.

Langmuir isotherm	q_m (mg/g)	114.8
	K_L (L/mg)	3.80
	χ^2	20.2
Freundlich isotherm	$1/n$	0.252
	K_F (L/g)	135.4
	χ^2	0.201
Redlich-Peterson isotherm	g	0.751
	B (L/mg)	3.2×10^4
	A (L/g)	1.9×10^6
	χ^2	0.280

3. 4. Effect of Contact Time

It is necessary to identify the step that governs the overall removal rate in the above sorption process. The pseudo-first order and pseudo-second order kinetic models were tested to fit the experimental data obtained for Hg(II) uptake by FTPC. The kinetic study results are given in Table 3 and Figure 5.

Pseudo-First Order Kinetic Model

A simple kinetic model which describes the process of sorption is the pseudo-first order equation suggested by Lagergren.[19,20]

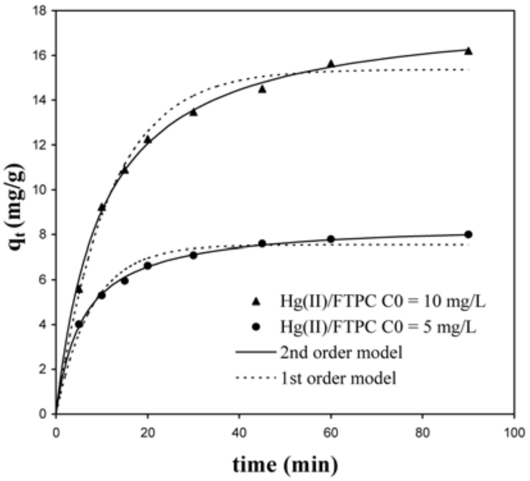

Figure 5: Fitted kinetic model for Hg(II) on FTPC system.

$$q_t = q_e\left[1-\exp(-k_1 t)\right] \tag{5}$$

The first order equation is applicable only for the initial 10 to 20 minutes of the sorption process. First order rate constant k_1 and equilibrium capacity q_e values are obtained from slope and intercept of the above plot. The q_e values calculated from the plots are lower than the experimental one. The removal of metal ions using FTPC does not follow the pseudo-first order equation.

Pseudo-Second Order Kinetic Model

The pseudo-second order kinetic equation was developed for the sorption process.[21]. The equation is given below:

$$q_t = q_e\left(\frac{q_e k_2 t}{1+q_e k_2 t}\right) \tag{6}$$

There are 3 consecutive steps taking place in the sorption of a sorbate by a porous sorbent:

1. transport of the sorbate to the external surface of the sorbent (film diffusion)
2. transport of the sorbate within the pores of the sorbent (particle diffusion)
3. sorption of the sorbate on the interior surface of the sorbent (pore diffusion)

The rate of the reaction is mainly controlled by the first two steps. The plots of time vs. q_t are shown in Figure 6. The χ^2 values for the non-linear plots of pseudo-second order plots are lower (0.0085 and 0.045 for 5, 10 mg/L dye solution respectively) than the pseudo-first order reaction plots (0.159 and 0.152). This shows that the pseudo-second order kinetic model explains the sorption in a better way. Increase of initial dye concentration from 5 to 10 mg/L increases the initial rate constant ‘h’ from 1.52 to 1.82 mg/g min and the pseudo second order rate constant value k_2 decreases from 0.02 to 0.00558 g/mg

Table 3. Parameters for the fitted kinetic models for the FTPC-Hg(II) system.

		Pseudo-first order model	
C_0 mg/L	q_1 mg/g	k_1 1/min	χ^2
5	7.50	0.129	0.159
10	15.4	0.0859	0.152

Pseudo-second order model

q_e mg/g	k_2 g/mg min	h mg/g min	χ^2
8.10	0.0200	1.45	0.00855
17.5	0.00558	1.82	0.0471

min. Similar decrease in k values with increase in metal ion concentration is reported by other researchers[22] also. This is due to the decrease in the readily available vacant adsorption sites as the metal ion concentration is increased. In other words, once the easily available activated sites are occupied the excess metal ions in solution find remote adsorption sites inside the pores of the carbon with difficulty.

3. 5. Desorption Study

Desorption of Hg(II) from the spent carbon was also carried out with various concentration of HCl and KI solutions to recycle the spent carbon. The results are given in the Figure 6. The figure shows the percentage of desorption increases with decreasing the pH of the solution and reached 93% using 100 ml of water having pH = 1. This is mainly due to ion exchange process and 98% removal by 100 mL of 3% KI solution. The maximum recovery by 3% KI solution is due to the formation of more table tetraiodo mercury (II) complex.[23]

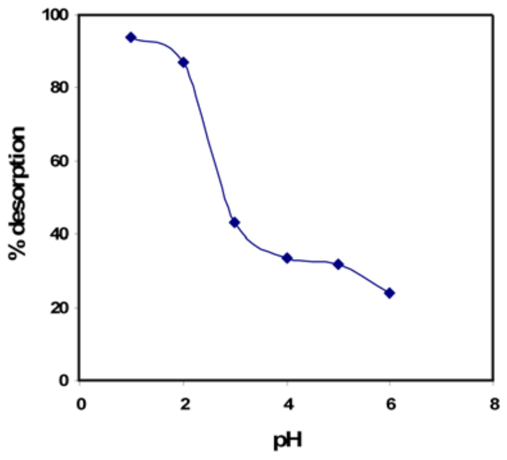

Figure 6: Desorption study at various pH

4. Conclusion

The adsorption kinetics and isotherm of Hg(II) removal using FTPC was carried out in batch experimental system. The following conclusions can be drawn based on the above study. The adsorption strongly depends on the parameters such as initial concentration of Hg(II), pH, carbon dose and contact time. The rate of adsorption follows pseudo second order rate equation. The spent carbon can be reused. The desorption studies showed that the percentage of removal increasing with decreasing the pH of water and 3% KI solution. So FTPC can be employed for the removal of Hg(II) from wastewater.

5. References

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Povzetek

Proučevali smo adsorpcijo Hg(II) iz vodnih raztopin na aktivnem oglju, pridobljenem iz strokov ognjenega drevesa (*Delonix regia*), obdelanih s žveplovo (VI) kislino. Izkazalo se je, da proces adsorpcije sledi hitrostnemu zakonu psevdo 2. reda. Adsorpcijo lahko opišemo s Freundlichovo in Redlich-Peterson izotermo in je močno odvisna od začetne koncentracije Hg(II), pH, količine oglja ter kontaktnega časa. Adsorbiran Hg(II) lahko desorbiramo s spiranjem s kislo 3 % raztopino KI.