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Adsorptive Removal of Mercury(II) Ions from Water and Wastewater by Polymerized Tamarind Fruit Shell

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Abstract: A novel adsorbent, formaldehyde polymerized tamarind fruit shell (FPTFS) containing sulphonic acid functional groups was prepared and its utility for Hg(II) adsorption from water and wastewater was investigated. The kinetic and isotherm data, obtained at optimum pH value 6.0 for different concentrations and temperatures, could be fitted with the Ritchie modified second-order equation and Sips isotherm model respectively and the coefficients indicated favorable adsorption of Hg(II) on the FPTFS. The complete removal of 23.86 mg/L Hg(II) from chlor-alkali industry wastewater was achieved by 4 g/L FPTFS. The reusability of the FPTFS for several cycles was also demonstrated using 0.1 M HCl solution.

Keywords: Desorption, isotherm, mercury(II) adsorption, tamarind fruit shell, thermodynamic parameters

INTRODUCTION

The ion exchange capacity and general sorptive characteristics of lignocellulosics for heavy metal ions removal from wastewater is well acknowledged. Most of the lignocellulosic biopolymers contain cellulose, hemicellulose, pectin, lignin, tannin, and organic extractives. The polyphenolic compounds such as lignin and tannin present in lignocellulosics is believed to be the active sites for attachment of heavy metal cations

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(1,2). The application of these materials as such will cause certain problems such as lower durability, leaching of soluble organic components at strong acidic and basic media, lower selectivity, and adsorption capacity. Chemical modification of these lignocellulosic materials is one possible solution to resolve all these defects. Recently many types of chemical modifications were reported in the literature such as acid activation, polymer grafting, alkali treatment, cross linking, and cationization methods which can enhance the physico-chemical properties and uptake capacity of the natural biosorbent (3–7). Many functionalized lignocellulosics, acting as cation exchangers were prepared from natural materials such as news paper pulp (8), coconut shell (9), gum arabic (10), oak saw dust (3), saw dust and modified pea nut husk (11), Pinus radiata bark (12), and coir pith (13) and their feasibility to remove metal ions from aqueous solutions were reported in literature.

Tamarind fruit shell (TFS) is an easily available agricultural waste derived from the Tamarind plant (*Tamarindus indica*). The utility of this waste residue in comparison to other agricultural wastes like sawdust, rice husk, and coir pith, is not yet exploited fully and in some parts of India, it is simply used as a solid fuel. In the present work the applicability of this agro waste residue for metal ion removal from aqueous solutions is investigated. The TFS was polymerized using formaldehyde in the presence of sulphuric acid to form sulphonic acid functionalized cation exchanger (FPTFS) and the chemical modification was analyzed using FTIR spectra. The feasibility of FPTFS was tested by its capacity to remove Hg(II) ions from aqueous solutions. Hg(II) is selected as a representative metal ion because it is a pervasive contaminant that is highly toxic and is readily accumulated by organisms. The major effects of mercury poisoning are neurological and renal disturbances, impairment of pulmonary function, chest pain, and dyspnousea. Dispersion of mercury into water streams occurs from industries such as chlor-alkali, paint, pulp and paper, oil refining, electrical, rubber processing, and fertilizer. The permissible limit of mercury in drinking water according to Indian Standard Institution (ISI) is 0.001 mg l^{-1} (14) and in discharge effluents from industries should be 0.01 mg l^{-1}. Hence, it is necessary to remove Hg(II) ions from wastewaters before they are discharged into the environment.

The batch adsorption process was carried out to optimize the operational parameters affecting Hg(II) adsorption such as initial pH, contact time, initial concentration, adsorbent dose, and temperature. The equilibrium and kinetic data were analyzed using different isotherm and kinetic models. The kinetic and isotherm parameters and the best-fit model were demonstrated by the non-linear regression method using Solver add-in with Microsoft's spreadsheet, Microsoft Excel by minimizing the hybrid error function (HYBRID) as (15):

$$\mathrm{HYBRID}(\%) = \frac{100}{n-p}\sum_{i=1}^{p}\left[\frac{(q_{\mathrm{exp}} - q_{\mathrm{cal}})^2}{q_{\mathrm{exp}}}\right]_i \tag{1}$$

where n is the number of data points and p is the number of parameters within the equation. The activation and thermodynamic parameters affecting adsorption were determined. In addition, the adsorption/desorption cycles were conducted using 0.1 M HCl to explore its durability and suitability for the design of continuous batch reactor.

EXPERIMENTAL PROCEDURE

Adsorbent Preparation

The TFS used for the preparation of the adsorbent was collected from a local market, washed with distilled water to remove the surface impurities, and dried at 80°C in an oven. The dried TFS was powdered and particles of 80–230 mesh size were used for chemical modification. Two parts of TFS was treated with 20 parts of 0.2 N H_2SO_4 and five parts of 39% HCHO. The reaction mixture was heated in a water bath at 60°C for 6 h and stirred vigorously. The polymerized TFS (FPTFS) was filtered, washed repeatedly with distilled water and dried at 60°C. The dried FPTFS was powdered, sieved, and particles of 80–230 mesh size (0.096 mm) were used for batch studies.

Hg(II) Solutions

All chemicals used were of analytical grade. A stock solution of Hg(II) (1000 $\mathrm{mgl^{-1}}$) was prepared by dissolving 1.35 g $HgCl_2$ (Fluka, Switzerland) in 1000 ml distilled water. Other working solutions with Hg(II) concentrations ranging from 25 to 600 $\mathrm{mg\ l^{-1}}$ were prepared by appropriate dilution of the stock solution. The pH of the working solutions was adjusted to the desired value by the addition of 0.1 M HCl or 0.1 M NaOH solutions.

Analysis

The FTIR spectra of TFS and FPTFS were obtained using the pressed disc technique in a Perkin Elmer IR–180 Spectrophotometer. The pH measurements were done by Systronic microprocessor pH meter (model μ 362; India). The point of zero change (pH_{pzc}) of TFS and FPTFS were determined by potentiometric titration method (16). The apparent density of the adsorbents was also determined by specific gravity bottle (10 ml capacity) using nitrobenzene as a displacing liquid. The cation-exchange capacity (CEC) was determined by the column process using 1.0 M $NaNO_3$ as the eluent at a flow rate of 0.5 ml min^{-1} (17). Chemical oxygen demand (COD) in aqueous solution was determined by means of the dichromate method (18). A temperature controlled water bath flask shaker (Labline, India) was used for shaking all the solutions. The concentration of metal ions in the solution was determined using a GBC Avanta A 5450 (Australia) Atomic Absorption Spectrophotometer (AAS).

Adsorption Experiments

The adsorption experiments were conducted by shaking 100 mg of FPTFS with 50 ml of Hg(II) solutions with different initial concentrations ranging from 25 to 600 mg l^{-1} in 100 ml Erlenmeyer flask at 200 rpm rpm in a water bath shaker at fixed temperature. The effect of pH on the adsorption of Hg(II) ions onto FPTFS was studied at initial concentrations of 25 and 50 mg l^{-1} by adjusting the pH value between 2.0 and 8.0 using 0.1 M NaOH and HCl. The effect of chemical modification on adsorption potential was analyzed with different adsorbent doses of TFS and FPTFS with an initial concentration of 25 mg l^{-1}. The effects of contact time and initial Hg(II) ion concentration on Hg(II) adsorption were investigated by shaking FPTFS with 50, 100, 150, and 200 mg l^{-1} Hg(II) solutions at pH 6 for 180 min and at 30°C. Also, kinetic experiments were done at the temperature range 30–60°C with 200 mg l^{-1} Hg(II) solution. Isotherm experiments were conducted at 30°C with initial concentrations ranging from 50 to 600 mg l^{-1}. The utility of the adsorbent was estimated for removal of Hg(II) from chlor-alkali industry wastewater. In all these batch processes, the supernatants after attaining equilibrium were removed by centrifugation and the metal ion concentration was determined using AAS. The amount of Hg(II) adsorbed, q_e (mg g^{-1}) was calculated using the equation

$$q_e = (C_o - C_e)\frac{V}{m} \tag{2}$$

where C_o and C_e are the initial and equilibrium Hg(II) concentrations (mg l^{-1}) respectively, m is the mass of FPTFS (g) and V is the volume of the solution.

Desorption Experiments

In order to determine the reusability and durability of FPTFS, consecutive adsorption-desorption cycles were performed four times by using the same adsorbent. Hg(II) was loaded on FPTFS by treating 100 mg with 50 ml of 25 mg l^{-1} Hg(II) solution. The Hg(II) loaded FPTFS was then stirred with 50 ml of 0.1 M HCl for 3 h. The final Hg(II) concentration in the aqueous phase was determined using AAS. The desorption percentage was calculated using the following equation

$$\text{Description}(\%) = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

The chemical modification of TFS and Hg(II) – FPTFS interactions were followed using FTIR spectroscopy. The FTIR spectra of TFS, FPTFS, and Hg(II)-loaded FPTFS was shown in Fig. 1. The intense absorption peak around 3400 cm^{-1} show the presence of hydroxyl groups as part of cellulose structure and polyphenols originally present on TFS. An absorption band at 2925 cm^{-1} in TFS can be assigned to the in phase stretching vibration of $-CH_{2-}$ alkane from cellulose and hemicellulose. The characteristic band 1066 cm^{-1} originates from the C–O stretching vibration of –C–OH group. The absorption band at 1730 cm^{-1} for FPTFS corresponds to the C=O stretching of –COOH group. Bands at 677 cm^{-1} for TFS and 673 cm^{-1} for FPTFS arises from β-glucosidic linkage. Additional peaks at 1185, 1135, and 605 cm^{-1} were observed for

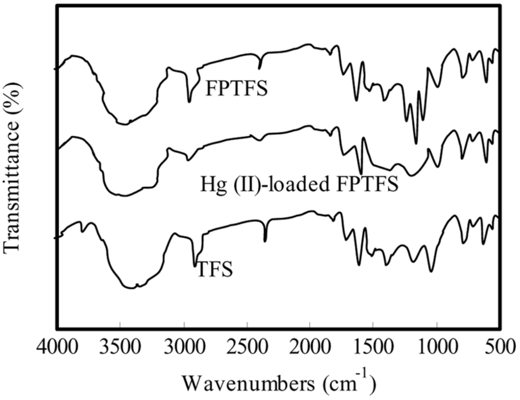

Figure 1. FTIR spectra of TFS, FPTFS and Hg(II) loaded FPTFS.

FPTFS showing the presence of $-SO_3H$ group. Some peaks in FPTFS after adsorption show lower intensities and also exhibit small differences in frequencies indicating the participation of these functional groups in the adsorption of Hg(II) by FPTFS. The major changes are, the band at 1033 cm^{-1} disappeared after Hg(II) adsorption in Hg(II)–FPTFS, 1730 cm^{-1} peak shifted to 1710 cm^{-1} with lower intensity and 1185, 1135, and 605 cm^{-1} bands were shifted to a slightly lower frequency region with an appreciable reduction in intensity. This clearly confirms that the sulphonate and carboxylate functional groups present on FPTFS were mainly responsible for Hg(II) adsorption.

The physico-chemical characteristics of TFS and FPTFS are shown in Table 1. The chemical modification of TFS caused increased surface area for FPTFS due to the reduction in the crystalline domains in TFS through formaldehyde treatment in the presence of 0.2 N H_2SO_4. The cation exchange capacity and total acidity of TFS increased in FPTFS due to the introduction of carboxylate and sulphonate functional groups through chemical treatment. The pH_{pzc} shifted from 7.4 in TFS to 5.4 in FPTFS showing that chemical modification made FPTFS surface more negative facilitating better Hg(II) adsorption.

Effect of Surface Modification

The effect of surface modification on Hg(II) adsorption was studied by conducting batch experiments using an initial concentration of 25 mg l^{-1} with varying adsorbent doses of TFS and FPTFS. Figure 2 shows that the percentage of adsorption increased with increase in adsorbent doses and for the quantitative removal of 25 mg Hg (II) from 1000 ml aqueous solution, a minimum adsorbent dosage of 2.5 g FPTFS or 4 g TFS was required. The increase in removal percentage with doses may be due to the availability of more adsorption sites at high doses. The results clearly show that FPTFS is 1.6 times more effective than TFS for Hg(II) removal

Table 1. Adsorbent characterization

Parameter	TFS	FPTFS
Surface area ($m^2 g^{-1}$)	76.2	95.2
Cation exchange capacity (meq g^{-1})	0.43	1.33
Total acidity (meq g^{-1})	0.53	1.48
Apparent density ($g l^{-1}$)	1.02	1.32
pH_{pzc}	7.4	5.4
Particle size (mm)	0.096	0.096

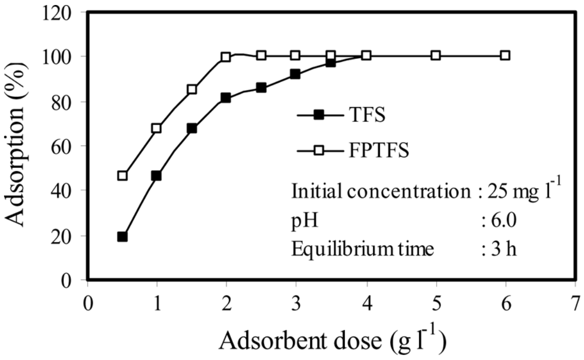

Figure 2. Effect of adsorbent dose on the removal of Hg(II) from aqueous solution by TFS and FPTFS.

from aqueous solutions. The high percentage removal obtained for FPTFS may be due to the stability provided by formaldehyde polymerization and also due to the introduction of –SO_3H group on the FPTFS surface through chemical treatment. The values of pH_{pzc} of TFS and FPTFS were found to be 7.4 and 5.4 respectively. The low pH_{pzc} of FPTFS indicates that the FPTFS surface became more negative due to chemical treatment and this increases the extent of Hg(II) adsorption onto FPTFS.

The amount of COD in water after chemical treatment with different amounts of TFS and FPTFS was also determined. When the adsorbent dose increased from 0.5 to 6.0 g l^{-1}, the values of COD increased from 29.9 to 311.2 mg l^{-1} in Hg(II) solutions treated with TFS, whereas for FPTFS the values increased from 5.2 to 28.7 mg l^{-1}. In the latter case, the COD in water was within the range of COD of water used for domestic applications. Formaldehyde treatment induces the stabilization of the hydrolysable compounds of TFS by creating new bonds to constitutive units, and makes the TFS able to adsorb metal ions without an increase in COD that is due to release of phenolic compounds. Huang et al. (19) reported that lignin is more sensitive than cellulose to polymerization. Lignin generally contains a relatively high concentration of the P-hydroxyphenylpropane group and also variable quantities of syringyl and guaiacyl groups (20). The sensitive component for formaldehyde polymerization might be the phenolic hydroxyl groups of lignin present in TFS. Formaldehyde reacts with phenolic hydroxyl group to form phenol-formaldehyde like resin and in the presence of sulphuric acid, sulphonyl groups are introduced in the polymer matrix. Since FPTFS possess high adsorption capacity relative to TFS, further batch studies were done only with FPTFS.

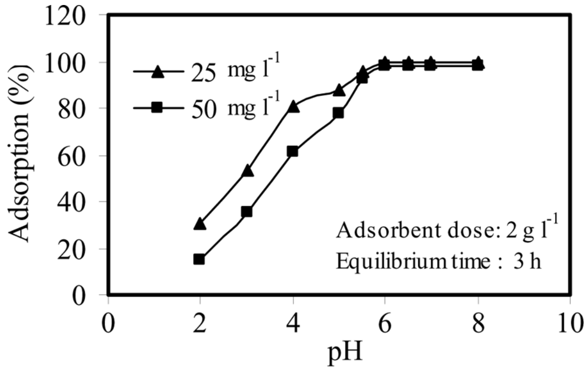

Figure 3. Effect of pH on the adsorption of Hg(II) onto FPTFS.

Effect of pH

The effect of solution pH on Hg(II) adsorption is shown in Fig. 3. The figure shows that, the amount of Hg(II) ions adsorbed increased sharply with pH values up to 6.0 and after 6.0 a plateau is obtained. The maximum adsorption capacity at pH 6.0 was found to be 99.5% and 97.7% for initial concentration of 25 and 50 mg l^{-1}. At low pH values the adsorption capacity is very low. Anirudhan et al. (21) have investigated adsorption of Hg(II) ions onto cationic exchange resin of carboxyl banana stem and they reported that maximum adsorption was achieved in the pH range 6.0–9.0. However, studies done by Atia (22) and Donia et al. (23) the best pH for the adsorption of Hg(II) onto modified chitosan and Schiff base modified magnetic chitosan resin was 6.0 and 8.0, respectively. Vazquez et al. (24) reported that maximum adsorption was obtained at pH 8.0 in their Hg(II) adsorption studies using formaldehyde treated pinus pinaster bark. The low adsorption capacity at low pH is apparently due to the presence of higher concentration of H_3O^+ ions in the solution which compete with the Hg(II) ions for the adsorption sites of FPTFS. When the pH is increased, H_3O^+ concentration in the solution decreases but Hg(II) ion concentration remains same leading to increased uptake.

On considering the pH_{pzc} of FPTFS and the existence of Hg(II) in different ionic states in the solution another plausible explanation for Hg(II) adsorption can be provided. In the regions of high adsorption capacity (pH: 5.5–8.0), the dominant metal species are Hg^{2+} and $Hg(OH)^+$ ions. At a pH below 5.4 (pH_{pzc}), the FPTFS surface is positively charged due to the protonation of active sites and this protonation effect will be more pronounced at low pH values due to the presence of high concentration of H^+ ions in the solution. During adsorption, the pH value of solution decreases and this is possible only by the release of H^+ ions from the surface of FPTFS. This data clearly reflects the fact that below pH_{pzc}, the adsorption occurs through ion exchange process as:

$$2H - FPTFS + Hg^{2+} \longrightarrow (FPTFS)_2Hg + 2H^+ \tag{4}$$

$$H - FPTFS + Hg(OH)^+ \longrightarrow FPTFS - Hg(OH) + H^+ \tag{5}$$

Above pH_{pzc}, the FPTFS surface is having negative charge and the positively charged Hg^{2+} and $Hg(OH)^+$ species gets adsorbed through electrostatic interaction. Due to the precipitation of Hg(II) ions at higher pH values, experiments were limited upto pH 8.0 only. Since maximum removal occurred at pH 6.0, the optimum pH for Hg(II) adsorption was selected as 6.0.

Effect of Contact Time and Initial Concentration

The time dependence study of metal ion adsorption using different Hg(II) ion concentrations were conducted to determine the equilibrium time needed for adsorption and also to investigate the nature of adsorbate-adsorbent interactions responsible for adsorption. Figure 4 shows the adsorption of Hg(II) ions as a function of contact time at different initial concentrations. About 80% removal was achieved within about 60 min and thereafter the adsorption was gradual and equilibrium was attained at 3 h. The initial faster rate of Hg(II) ion adsorption may be due to the large number of adsorption sites available for adsorption and the subsequent decrease in adsorption rate is probably due to the saturation of the active sites and attainment of equilibrium. For different initial concentrations there is no appreciable variation in contact time needed to attain equilibrium. Thus the equilibrium time is found to be independent of initial concentration. Relatively short equilibrium time coupled with high removals is considered as an initial indication that the adsorption of Hg(II) ions is a chemical-reaction controlled, rather than diffusion controlled process (25). Several studies of Hg(II) adsorption onto various adsorbents have shown a wide range of adsorption rates. Atia (22) reported that Hg(II) adsorption by modified chitosan resin was rapid during the first 80 min, 90% removal achieved in this time period and reached its equilibrium with complete removal in 2 h. Donia et al. (23) reported that equilibrium was achieved in 70 min in their Hg(II) adsorption kinetic studies, in which they have used Schiff base modified magnetic chitosan. Say et al. (26) investigated the adsorption of Hg(II) by dithiocarbomate-anchored polymer/organosmectite composites and

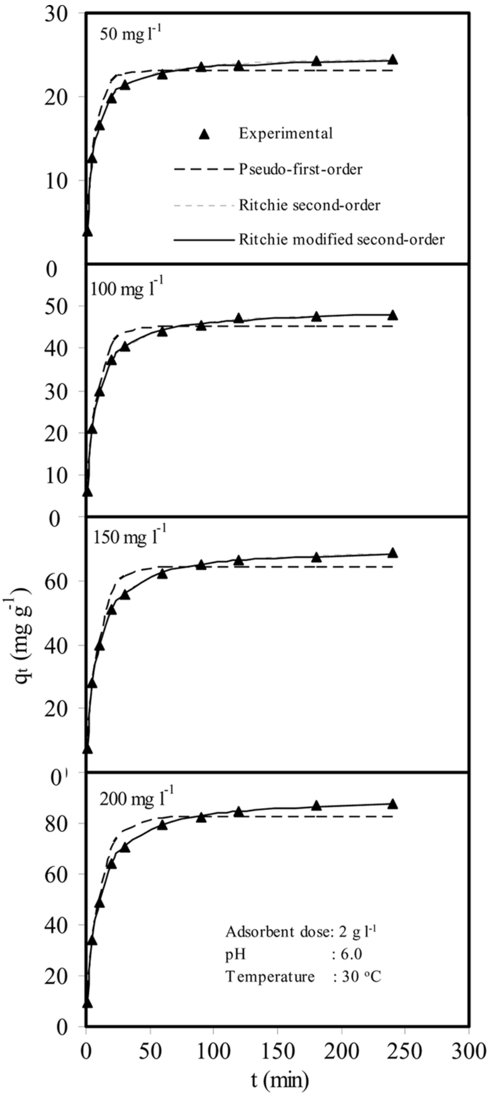

Figure 4. Adsorption profiles of Hg(II) on FPTFS in relation to the contact time, at different initial concentrations and comparison of different kinetic models.

reported a 60 min equilibrium time for the adsorption. Vazquez et al. (24) have used formaldehyde treated pinus pinaster bark for the adsorption of Hg(II) ions and they reported that adsorption was completed in 24 h. In this case, they proposed an ion exchange mechanism in which hydroxyl proteins of the procyanidin units of the tannins in the bark are exchanged with Hg(II) ions from aqueous solutions. All these studies published in the literature have been carried out under different experimental conditions; hence it is too difficult to compare the equilibrium times reported. However, the equilibrium time of 3 h in the case of FPTFS which seems to be satisfactory. Hence, the equilibrium time was maintained at 3 h in subsequent analysis.

For an initial concentration of 50, 100, 150, and 200 mg l^{-1} of Hg(II), at 30°C, the adsorption capacity was found to be 24.42, 47.78, 68.95, and 87.94 mg g^{-1}respectively. The data show that the adsorption capacity increases with increase in initial concentration. Higher initial concentrations create a high concentration gradient near the adsorbent surface and this concentration gradient provides a greater driving force for the Hg(II) ion adsorption. The percentage adsorption of Hg(II) ions on FPTFS decrease from 97.7 to 87.9% as the initial Hg(II) concentration increased from 50 to 200 mg l^{-1}. At lower concentrations, all Hg(II) ions in the solution can interact with the adsorption sites of FPTFS and hence the percentage of adsorption was higher but at higher initial concentrations, saturation of adsorption sites causes lower adsorption yield. Therefore the purification yield during the adsorption process can be increased by diluting the wastewater containing high metal ion concentration.

Effect of Temperature

Temperature is a parameter holding great significance in the adsorption process. The effect of temperature on Hg(II) adsorption was studied by conducting batch experiments at different temperatures 30, 40, 50, and 60°C with an initial concentration of 200 mg l^{-1} and the results are shown in Fig. 5. The sorption capacity increased from 87.94 mg g^{-1} to 93.84 mg g^{-1} when the temperature of the solution increased from 30 to 60°C. The fact that adsorption of Hg(II) is favored at high temperature indicated that the mobility of Hg(II) ions increased with rise of temperature and hence it should interact more efficiently with the sorbent surface. The increase in sorption capacity with increase in temperature indicates that the Hg(II) adsorption process by FPTFS is endothermic in nature and is also an activated process. The endothermic nature of metal adsorption has also been reported for the adsorption of Hg(II) ions onto polyaniline/polystyrene composite (27) and polyacrylamide grafted coir pith (13). However, adsorption of Hg(II) ions onto Schiff base-modified magnetic chitosan resin has been reported to be an exothermic process (23).

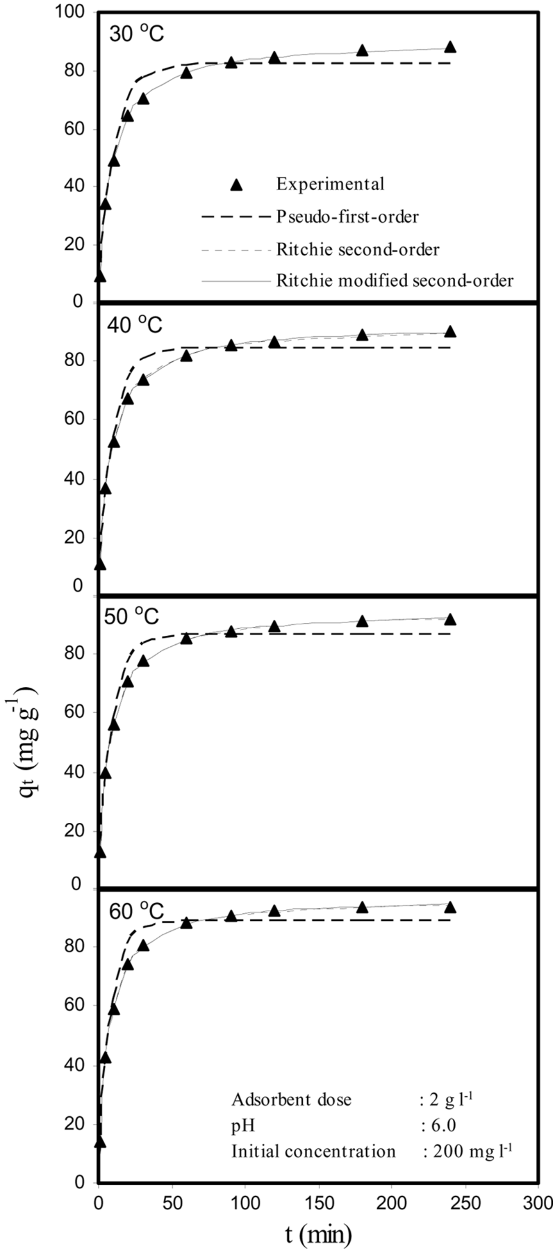

Figure 5. Adsorption profiles of Hg(II) on FPTFS in relation to the contact time, at different temperatures and comparison of different kinetic models.

Adsorption Kinetics

The kinetic data at different initial concentrations and temperatures were modeled using pseudo-first-order (28) (Eq. (6)), Ritchie second- order (29) (Eq. (7)) and Ritchie modified second- order (30) (Eq. (8)) kinetic models to find out the model that best describes the experimental data and also to access the nature of adsorption process.

$$q_t = q_e(1 - e^{-kjt}) \tag{6}$$

$$q_t = q_e\left\{1 - \left[\frac{1}{1 + k_2 t}\right]\right\} \tag{7}$$

$$q_t = q_e\left\{1 - \left[\frac{1}{\beta + k_{2_m} t}\right]\right\} \tag{8}$$

where q_e and q_t are the amounts of Hg(II) ion adsorbed (mg g^{-1}) at equilibrium and time 't' respectively. k_1, k_2 and k_{2m} are the Lagergren, Ritchie second-order, and Ritchie modified second-order rate constant of adsorption respectively. β is a constant representing the initial particle loading. The kinetic parameters of these models at different initial concentrations and temperatures were determined using nonlinear optimization method by minimizing the hybrid error function (HYBRID) and the results are presented in Tables 2 and 3. The lower HYBRID values for Ritchie modified second-order model at different concentrations and temperatures indicate that this model best describe the kinetic data than pseudo-first-order and Ritchie second-order models. A comparison between the experimental and calculated values using different models at different concentrations and temperatures is shown in Figs. 4 and 5.

The values of k_{2m} decreased from 2.06×10^{-1} to 1.20×10^{-1} g mg^{-1} min^{-1}, while the initial particle loading (β) and equilibrium sorption capacity (q_e) increased from 0.977 to 0.999 and 24.79 to 90.51 mg g^{-1} respectively when the initial Hg(II) concentration increased from 50 to 200 mg l^{-1} (Table 2). As the temperature increased from 30 to 60°C, the values of k_{2m} increased from 1.20×10^{-1} to 1.57×10^{-1} g mg^{-1} min^{-1}. The initial particle loading (β) and equilibrium sorption capacity (q_e) increased from 0.999 to 1.010 and 90.51 to 97.13 mg g^{-1} respectively with rise in temperature from 30 to 60°C. The increase in k_{2m} value with temperature clearly shows that Hg(II) adsorption on FPTFS is more favorable at higher temperature i.e., for the sorption of Hg(II) ions energy is required and hence is considered as an endothermic process. The applicability of Ritchie modified second-order model implies that, a single sorbate ion occupies two adsorption sites of adsorbent during adsorption process.

Table 2. Kinetic parameters for the adsorption of Hg(II) onto FPTFS at different initial concentrations

	Concentration (mg l^{-1})			
	50	100	150	200
q_{eexp}(mg g^{-1})	24.42	47.78	68.95	87.94
Pseudo-first-order				
K_1 (min^{-1})	0.146	0.113	0.099	0.094
q_{ecal} (mg g^{-1})	23.00	45.15	64.30	82.17
HYBRID	9.03	15.99	25.23	34.83
Ritchie Second-order				
K_2 (g mg^{-1} min^{-1})	0.194	0.146	0.126	0.120
q_{ecal} (mg g^{-1})	24.92	49.40	70.79	90.51
HYBRID	0.290	0.504	0.785	0.168
Ritchie Modified Second-order				
k_{2M} (g mg^{-1} min^{-1})	0.206	0.153	0.132	0.120
β	0.9778	0.9855	0.9856	0.9999
q_{ecal}(mg g^{-1})	24.79	49.17	70.42	90.51
HYBRID	0.100	0.221	0.236	0.193

Table 3. Kinetic parameters for the adsorption of Hg(II) onto FPTFS at different temperatures ($C_o = 200$ mg l^{-1})

	Temperature (°C)			
	30	40	50	60
q_{eexp} (mg g^{-1})	87.94	89.88	92.00	93.84
Pseudo-first-order				
K_1 (min^{-1})	0.094	0.104	0.111	0.120
q_{ecal} (mg g^{-1})	82.17	84.14	86.71	89.12
HYBRID	34.83	39.06	37.17	38.91
Ritchie Second-order				
K_2 (g mg^{-1} min^{-1})	0.120	0.135	0.147	0.162
q_{ecal} (mg g^{-1})	90.51	92.15	94.57	96.82
HYBRID	0.168	0.242	0.516	0.555
Ritchie Modified Second-order				
k_{2M} (g mg^{-1} min^{-1})	0.120	0.132	0.142	0.157
β	0.9999	1.0084	1.0108	1.0109
q_{ecal} (mg g^{-1})	90.51	92.41	94.89	97.13
HYBRID	0.193	0.029	0.223	0.310

Activation Parameters

The values of k_{2m} obtained at different temperatures can be applied in Arrhenius equation to determine the adsorption activation energy as:

$$\ln k_{2m} = \ln k_0 - \frac{E_a}{RT} \tag{9}$$

where k_0 is the Arrhenius frequency factor, E_a is the activation energy, *R* is the gas constant, and T is the solution temperature (K). E_a value calculated from the slope of the linear plot of ln k_{2m} versus 1/T (figure not shown) was found to be 7.32 kJ mol^{-1}. The E_a in the range 5–40 kJ mol^{-1} corresponds to physisorption and in the range 40–800 kJ mol^{-1} represents chemisorption (31). The low E_a value reflects a physisorption mechanism for Hg(II) adsorption on FPTFS. The other kinetic activation parameters were calculated using the Eyring equation as:

$$\ln\frac{k_{2m}}{T} = \left[\ln\frac{kb}{h} + \frac{\Delta S^{\neq}}{R}\right] - \frac{\Delta H^{\neq}}{RT} \tag{10}$$

where k_b is the Boltzmann constant, h is planck's constant, T is the temperature (K), $\Delta S^{\neq}$ is the entropy of activation, and $\Delta H^{\neq}$ is the enthalpy of activation. Plots of $\ln(k_{2m}/T)$ versus 1/T were found to be linear (figure not shown) and the values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ were obtained from the slope and intercept of this plot. The free energy of activation $\Delta G^{\neq}$ can be calculated as $\Delta G^{\neq} = H^{\neq} - T\Delta S^{\neq}$. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for Hg(II) adsorption were found to be 4.68 kJ mol^{-1} and -49.64 J mol^{-1} K^{-1} respectively. The positive value of $\Delta H^{\neq}$ suggests the endothermic adsorption process and the negative value of $\Delta S^{\neq}$ implies that the adsorption process bring in a more order near the adsorbent/adsorbate interface through the formation of an activated complex. The values of $\Delta G^{\neq}$ were found to be 19.72, 20.22, 20.72, and 21.21 kJ mol^{-1} at 30, 40, 50, and 60°C respectively. Since the sorption capacity increases with increase in temperature, more energy is required to metal binding on FPTFS, and hence the free energy of activation increases with increase in temperature.

Isotherm Analysis

The adsorbate-adsorbent interactions and the surface properties of the adsorbent were studied by isotherm modeling. In the present study the equilibrium data at 30°C were modeled using Langmuir, Freundlich, and Sips models. In order to optimize the design of a sorption system to remove Hg(II) from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. The best isotherm model is determined by nonlinear optimization method by minimizing the hybrid error function.

The Langmuir isotherm model assumes that the adsorption takes place at specific homogeneous sites within the adsorbent and it assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. The Langmuir isotherm is expressed as

$$q_e = \frac{q_{m_L} K_L C_e}{1 + K_L C_e} \tag{11}$$

where q_e is the adsorbed amount at equilibrium ($mg\,g^{-1}$), C_e the equilibrium concentration of the adsorbate ($mg\,l^{-1}$), q_{m_L} is the Langmuir monolayer sorption capacity ($mg\,g^{-1}$) and K_L is the Langmuir equilibrium constant ($l\,mg^{-1}$). The Langmuir equilibrium adsorption curve for Hg(II) adsorption on FPTFS at 30°C is given as

$$q_e = \frac{18.64 C_e}{1 + 0.14 C_e} \tag{12}$$

The Freundlich isotherm model is an empirical equation employed to describe heterogeneous systems, and it is characterized by the heterogeneity factor $1/n_F$. The model can be written as

$$q_e = K_F {C_e}^{1/n_F} \tag{13}$$

where K_F is the Freundlich constant related to adsorption capacity ($mg\,g^{-1}$) and n_F is a constant indicative of intensity of adsorption. The Freundlich equilibrium curve for Hg(II) adsorption is

$$q_e = 30.00 {C_e}^{0.283} \tag{14}$$

The sips isotherm model is a combination of the Langmuir and Freundlich isotherm models. The Sips model takes the following form (32):

$$q_e = \frac{q_{m_S} (K_S C_e)^{m_S}}{1 + (K_S C_e)^{m_S}} \tag{15}$$

where q_{m_S} is the Sips maximum adsorption capacity ($mg\,g^{-1}$), K_S is the Sips equilibrium constant $(l\,mg^{-1})^{m_S}$ and m_S is the Sips model exponent. The Sips model exponent m_S indicates surface heterogeneity and for a highly heterogeneous system, the deviation of m_S value from unity will be higher. The Sips equilibrium curve for Hg(II) adsorption is

$$qc = \frac{26.88 Ce^{0.614}}{1 + 0.163 Ce^{0.614}} \tag{16}$$

Table 4. Adsorption isotherm constants for Hg(II) adsorption on FPTFS at 30°C

Langmuir	
q_{mS} (mg g^{-1})	132.89
K_L (l mg^{-1})	0.140
HYBRID	85.79
Freundlich	
K_F (mg$^{1\text{-}(1/n)}$ l$^{1/n}$ g^{-1})	30.00
n_F	3.52
HYBRID	108.56
Sips	
q_{mS} (mg g^{-1})	164.66
K_S(l mg^{-1})^{mS}	0.052
m_S	0.614
HYBRID	0.479

The three isotherm model parameters along with HYBRID values are listed in Table 4. The low HYBRID values suggested that Sips isotherm model best describes the equilibrium data. A comparison between the experimental and calculated values using different models at 30°C is depicted in Fig. 6. The Sips maximum adsorption capacity, equilibrium constant and model exponent were found to be 164.66 mg g^{-1}, 0.052 (l mg^{-1})^{mS} and 0.614 respectively. The Sips model exponent value indicates that the FPTFS surface is heterogeneous in nature and this surface heterogeneity is another factor favoring Hg(II) adsorption on FPTFS. By using the Sips model exponent value, the expression for the separation

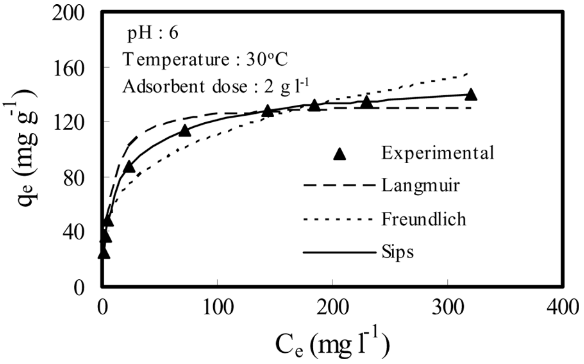

Figure 6. Comparison of different isotherm models to the experimental isotherm data for Hg(II) adsorption onto FPTFS.

factor R_S can be represented as (33)

$$R_S = \frac{1}{(1 + k_S(C_o)^{m_S})} \tag{17}$$

where C_o is the initial Hg(II) concentration ($mg\,l^{-1}$) in the solution. Based on the Sips model exponent value, the R_S values were determined. In the present study, the R_S value decreased from 0.633 to 0.273 with increase in concentration from 50 to 600 $mg\,l^{-1}$. This clearly shows that the sorption is more favorable at higher initial Hg(II) concentrations.

The Freundlich constant, K_F which is indicative of the adsorption capacity, was found to be 30.00. This value is very high compared to some of the values reported by other researchers for other type of adsorbents. For example, Ritchie et al. (34) studied the adsorption of Hg(II) on polycystine-functionalised cellulose filters and reported K_F value of 0.13. Vazquez et al. (24) have used formaldehyde treated pinus pinaster bark for the adsorption of Hg(II) ions and they reported K_F value of 1.48. The K_F values of the adsorption of Hg(II) ions on polyaniline/polystyrene composite (27) and thiol-grafted chitosan gel beads (35) were reported to be 0.158 and 7.59 respectively. The comparison of K_F value of FPTFS (30.00) used in the present study with those obtained in the literature shows that FPTFS is more effective for this purpose.

Test with Industrial Wastewater

Batch studies were conducted to evaluate the suitability of the adsorbent for wastewater treatment. Chlor-alkali industry wastewater collected from chlor-alkali plant situated in Kochi, India is used for this purpose. The composition ($mg\,l^{-1}$) of the wastewater is Hg^{2+}: 23.86; Pb^{2+}: 2.9; Cd^{2+}: 0.6; Mg^{2+}: 31.1; Ca^{2+}: 36.3; Na^{+}: 260.8; PO_4^{3-}: 13.1; NO_3^{-}: 17.1; NH_3: 27.1; Cl^{-}: 415.6; pH: 8.3; turbidity: 41.6; and conductivity ($mS\,cm^{-1}$): 19.1. The batch studies were conducted at different adsorbent doses and the results are presented in Fig. 7. Almost complete removal of Hg(II) ions was possible from 1000 ml solution with 4.0 g of FPTFS. These results were almost consistent with that obtained from batch experiments and this confirms that FPTFS is a very good adsorbent for the removal of Hg(II) ions from wastewater.

Design of Single Stage Batch Reactor

The adsorption isotherm data can be used to design a single stage batch adsorption system. The schematic diagram for a single-stage adsorption

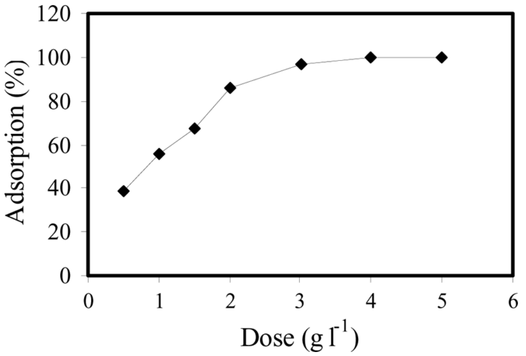

Figure 7. Effect of adsorbent dose on the adsorption of Hg(II) from chlor-alkali industry wastewater using FPTFS.

process is shown in Fig. 8. The solution to be treated contains V (l) of water and an initial Hg(II) concentration of C_o (mg l^{-1}), which is to be reduced to C_1 (mg l^{-1}) in the adsorption process. During the treatment process W (g) of FPTFS is added, and the Hg(II) concentration on FPTFS increases from q_o (initially) to q_e.

When the fresh adsorbent is used $q_o = 0$

The mass balance equating the Hg(II) removed from the liquid to that picked by FPTFS is

$$V(C_o - C_1) = W(qe - q_o) = Wq_c \tag{18}$$

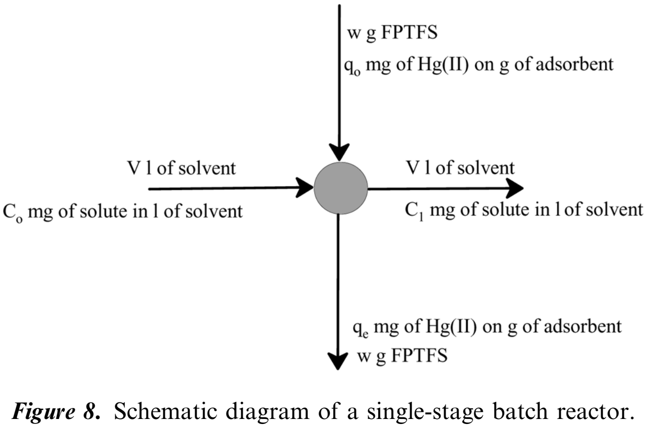

Figure 8. Schematic diagram of a single-stage batch reactor.

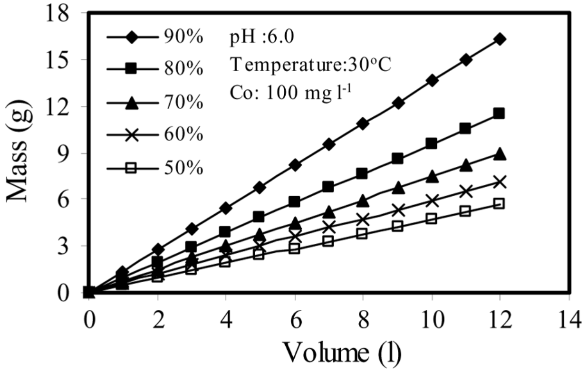

Figure 9. Mass of FPTFS (w) against Volume of Hg(II) solution (l) treated for different percentages Hg(II) removal.

Substituting for q_e from equation 16 and rearranging gives

$$\frac{W}{V} = \frac{C_o - C_1}{q_e} = \frac{(C_o - C_1)(1 + 0.163Ce^{0.614})}{26.88Ce^{0.614}} \tag{19}$$

This equation can be used to calculate the mass of FPTFS required to achieve a certain percentage removal by treating a definite volume of Hg(II) containing effluent having an initial concentration C_o. As an example, the mass of FPTFS required to treat Hg(II) solution having an initial concentration of $100\,\mathrm{mg\,l^{-1}}$ at 30°C and at pH 6.0 to achieve 50, 60, 70, 80, and 90% removal can be predicted from Equation 19 and the results are shown in Fig. 9.

Desorption Studies

The reusability of the FPTFS for Hg(II) adsorption was explored by conducting adsorption-desorption cycles using 0.1 M HCl as the desorbing agent. The desorption occurs by the replacement of metal ions by H^+ ions from the eluting acid. The adsorption-desorption cycles were repeated four times. During four cycles, the adsorption of FPTFS declined from 99.6% (12.45 mg g^{-1}) to 91.2% (11.40 mg g^{-1}) and the desorption of Hg(II) ions decreased from 98.4% (12.26 mg g^{-1}) to 88.7% (10.12 mg g^{-1}). The loss of FPTFS during four adsorption-desorption cycles were minimum and this behavior of FPTFS is highly beneficial for the design of batch reactors. A slight decrease in adsorption and desorption percentage during the repeated adsorption-desorption cycles also put some proof into the adsorption mechanism indicating that certain associative interactions are operating along with ion exchange process for Hg(II) removal from aqueous solutions.

CONCLUSIONS

This study investigated the adsorption potential of formaldehyde polymerized tamarind fruit shell (FPTFS) for Hg(II) adsorption from aqueous solutions. Several adsorption parameters such as pH, initial Hg(II) concentration, and temperatures have been investigated. The optimum pH for Hg(II) adsorption was 6.0 and the adsorption process attains equilibrium at 3 h. The Ritchie modified second-order model best described the kinetic data for different initial concentrations and temperatures. The increase in equilibrium uptake with temperature reflects endothermic nature of Hg(II) adsorption. The low E_a value ($7.32\,\mathrm{kJ\,mol^{-1}}$) reflects a physisorption mechanism for Hg(II) adsorption on FPTFS. The Sips isotherm model best describes the equilibrium data and the Sips model exponent value, m_S (0.614) indicates that FPTFS surface is heterogeneous in nature and is also favoring Hg(II) adsorption. The utility of FPTFS was checked using chlor-alkali industry wastewater. The experimental data were applied to design a single stage batch reactor. The adsorbed Hg(II) was desorbed quantitatively using 0.1 M HCl and four adsorption/desorption cycles were conducted. Certain associative interactions and ion exchange process are collectively responsible for Hg(II) adsorption on FPTFS.

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