

Preparation of an Adsorbent by Graft Polymerization of Acrylamide onto Coconut Husk for Mercury(II) Removal from Aqueous Solution and Chloralkali Industry Wastewater

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ABSTRACT: Graft copolymerization of acrylamide onto coconut husk (CH), initiated by the ferrous ammonium sulfate/H₂O₂ redox initiator system, was studied. To determine the optimum conditions of grafting, the effect of the concentrations of ferrous ammonium sulfate, the monomer, and H₂O₂ and the time and temperature on percentage of the graft yield was studied. A new adsorbent media having a carboxylate functional group was synthesized by the surface modification of polymer-grafted coconut husk (PGCH—COOH). The mechanism of graft polymerization and surface functionalization is proposed. The material exhibits a very high adsorption potential for Hg(II). The sorption of Hg(II) was found to be dependent on the contact time, concentration, pH, and temperature. Maximum removal of 99.4% with 2 g/L of the sorbent was observed at 125 $\mu\text{mol L}^{-1}$ Hg(II) concentration at pH 6.0. The slow step which determines the rate of exchange of Hg(II) ions is diffusion through the adsorbent particles. The diffusion coefficients, energy of activation, and entropy of activation were calculated and used to determine the theoretical behavior of the sorption process. The applicability of the Langmuir isotherm established the endothermic character of the adsorption. Acid regeneration was tried for several cycles with a view to recover the adsorbed metal ions and also to restore the sorbent to its original state. The adsorbent efficiency toward Hg(II) removal was tested using synthetic and chloralkali industry wastewaters. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1261–1269, 2000

Key words: graft polymerization; coconut husk; adsorption; mercury removal; wastewater

INTRODUCTION

Graft copolymerization on pure cellulose and natural lignocellulosic materials has received considerable attention because, in some cases, grafting yields copolymers with improved physicochemical properties with industrial and commercial value.^{1,2} Lignocellulose is a natural composite material that contains cellulose, hemicellulose, and lignin.

Coconut husk, the fibrous outer part of the coconut, basically contains lignin and cellulose.³ Huang et al.⁴ reported that lignin can accelerate grafting at the initial stage of reaction when Fe²⁺—H₂O₂ was used as the initiator. It was previously shown that the phenolic hydroxyl group of lignin accelerates the decomposition of H₂O₂ and the graft copolymerization of lignocellulose when Fe²⁺ ions are present in the system.⁵ Although much work on grafting of vinyl monomers onto wool,⁶ cotton,⁷ silk,⁸ and fibers⁹ has been reported, work on coconut husk has not been reported. The first part of the present research work

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deals with studies of the optimum conditions of grafting acrylamide onto coconut husk using the Fe^{2+} — H_2O_2 redox system.

The widespread use of mercury and its compounds in industrial and agricultural processes has led to their presence in large amounts in aquatic environments. The major industries discharging mercury through their effluents are the chloralkali manufacturing industry and paper and pulp, oil-refining, paint, pharmaceutical, and battery manufacturing industries. The tragic consequences of the toxicity of mercury were illustrated in the Minamata Bay area of Japan. Mercury causes damage of the central nervous system and chromosomes, impairment of pulmonary function and kidneys, and chest pains.¹⁰ Hence, it is necessary to remove Hg(II) from wastewaters before allowing the polluted water to mix with any part of the hydrosphere. The application of surface-modified adsorbents for the removal of trace-level toxic metals from aqueous media has received recent attention. Materials such as silica gel,¹¹ iron(III) oxide,¹² titanium(IV) oxide,¹³ tin(IV) oxide,¹⁴ and chitosan¹⁵ have already been used as polymer supports for the preparation of adsorbents. An anion-exchanger which could effectively remove anion contaminants has been developed from coconut coir dust.¹⁶ It was demonstrated in a previous article that carboxylate functional groups substituted in the backbone of polymerized material could act as adsorption sites for removing metals from solutions.¹⁷ Recently, we proposed a convenient procedure for a surface modification which involves the grafting of polyacrylamide onto sawdust using *N,N'*-methylenebisacrylamide as a crosslinking agent and subsequent functionalization of the polymer network with desired reagents.¹⁸ This article describes the preparation of a new adsorbent material based on polyacrylamide-grafted coconut husk having carboxylate functional groups. The adsorption properties of the adsorbent and its application to the treatment of Hg(II)-rich water and industrial wastewater are reported.

EXPERIMENTAL

Preparation of Adsorbent

All the reagents and solutions were prepared using reagent-grade chemicals from Fluka (Switzerland), BDH (UK), or Merck (Germany). Coconut husk (CH) was obtained from mature and dried

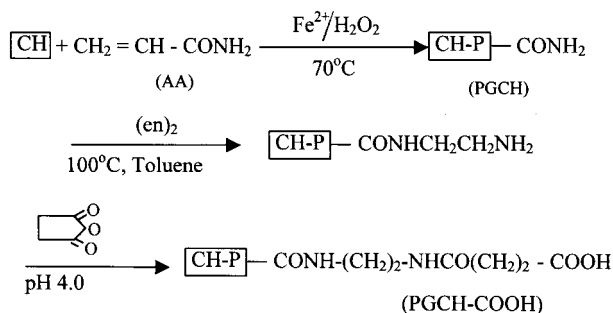
coconuts, which were collected during the summer from 10-year-old coconut palms in Mulloor situated near Kovalam Beach (Kerala, India). Samples of CH were reduced to pass through a 0.096-mm sieve before application of further treatments.

The CH was defatted with an ethanol–benzene (1:2 v/v) mixture in a Soxhlet apparatus for 12 h. After refluxing, the material was washed with ethanol and air-dried. Before initiating graft copolymerization, 1 g of CH was immersed in a 200-mL ferrous ammonium sulfate solution. A definite quantity of H_2O_2 and acrylamide (AA) was introduced into the reaction vessel at the desired temperature. After the specified time intervals, the reaction was arrested by quenching with ice-cold water. The homopolymer along with the polymer-grafted coconut husk (PGCH) were filtered off and washed with water. The homopolymer of acrylamide was extracted with water using the Soxhlet apparatus and then dried at 70°C. The percentage of graft yield was estimated from the following equation:

$$\% \text{ Graft yield} = \frac{\text{mass of graft copolymer} - \text{mass of substrate}}{\text{mass of substrate}} \times 100$$

The PGCH was refluxed with 25 mL of ethylenediamine (en)₂ in toluene for 8 h. To functionalize it with carboxylate groups, this material was refluxed with an equal mass of succinic anhydride in 1,4-dioxane at pH 4.0 for 6 h. The excess succinic anhydride was washed out with 1,4-dioxane and, finally, with alcohol and dried. The carboxylic acid-bound PGCH (PGCH—COOH) was ground and sieved to a 0.096-mm size.

The IR spectrum of PGCH—COOH (not shown) was recorded on a Bruker IFS 66V FTIR spectrophotometer. The broad peak centered at 3435 cm^{-1} is attributed to the overlapped bands arising from the $\nu\text{N—H}$ of the amide group and the $\nu\text{O—H}$ of the carboxylic group along with the OH stretching band from the support.¹⁹ The $\nu\text{C=O}$ of the amide group and the carboxylic group appeared as a composite peak¹⁹ centered at 1676 cm^{-1} . The absorption band at 2924 cm^{-1} is attributed to the contribution of C—H stretching from the CH_2 group. The peak at 1676 cm^{-1} ($\nu\text{C=O}$) along with another band at 1160 cm^{-1} , which is attributed to the C—O stretching band ($\nu\text{C—O}$) of the carboxylic group, indicate the presence of the —COOH group in the PGCH—



Scheme 1 Preparation of PGCH—COOH.

COOH.¹⁹ Based on these results, the structure of PGCH—COOH is represented in Scheme 1.

The surface area of the adsorbent was measured by the BET N₂ adsorption method using a surface-area analyzer (Quantasorb, Model-05/7). The porosity and the density of the adsorbent were determined by a mercury porosimeter and by a specific gravity bottle, respectively. The zero point of charge (pH_{zpc}) is defined as the pH of the suspension at which the surface charge density (σ₀) on PGCH—COOH is zero. To determine the pH_{zpc}, the potentiometric titration method was used.²⁰ The cation-exchange capacity of the adsorbent was determined by the sodium saturation method.²¹ About 1.0 g of the adsorbent was packed into a glass column (10 × 0.4 cm) and 100 mL of 0.1M NaNO₃ solution was percolated at the flow rate of 0.2 mL min⁻¹ through the column. The effluent in 10-mL fractions was collected and Na was determined using an Elico Model CL-136 (India) flame-emission spectrophotometer. The amount of the ions taken up by the adsorbent was evaluated from the difference between the initial and final concentrations of the ions in the solutions. The characteristics of the adsorbent are the following: particle size, 0.096 mm; surface area, 103.5 m² g⁻¹; porosity, 0.41 mL g⁻¹; density, 1.14 g mL⁻¹; cation-exchange capacity, 2.66 meq g⁻¹; and pH_{zpc}, 5.5.

Adsorption and Regeneration Studies

The adsorbate solution was prepared by dissolving Hg(NO₃)₂ in distilled water. Batch adsorption experiments were conducted by shaking an accurately weighed amount of the adsorbent (100 mg) with 50 mL of the Hg(II) solution of desired concentrations and pH in 100-mL stoppered bottles in a temperature-controlled water-bath shaker. The initial pH of the solution was maintained using 0.1M HNO₃ and NaOH solutions. The pH

was varied from 2 to 10. Constant stirring of the solution was maintained for a variable length of time. At predecided intervals of time, the test solutions were centrifuged to separate the adsorbent material from the solution and the supernatant was analyzed for aqueous Hg(II) ions using a spectroscopic method.²² Adsorption isotherms were measured at 30, 40, 50, and 60°C using solution concentrations ranging between 100 and 750 mg/L. The amount of Hg(II) removed was calculated by subtracting the Hg(II) concentration in the solution from the initial concentration.

For any adsorption process, the most important factors are the recovery of the adsorbent and regeneration capacity of the adsorbent. The adsorbed Hg(II) was eluted with 50 mL of 0.2M HCl. After mixing for 6 h, the supernatant liquid was centrifuged and the extract analyzed for Hg(II). A comparison of the value with the loss observed in the initial sorption step was used to compute the percentage recovery values. The sorbent sample thus regenerated was reused for adsorption purposes. The loading and regeneration cycle was repeated four times. After each cycle, the sorbent was washed with distilled water and dried.

RESULTS AND DISCUSSION

Graft Copolymerization

The optimum conditions for graft copolymerization of acrylamide onto CH were investigated by studying the effect of time, initiator, monomer, and temperature on the percentage graft yield. The effect of the variation of temperature on the graft yield was evaluated by keeping the concentrations of all the other reagents constant. The data indicate that the graft yield progressively increases with temperature (Fig. 1). Many factors may contribute to this variation of the graft yield with the temperature: (i) increase in the mobility of the monomer and initiator, (ii) higher rate of diffusion of the monomer and initiator from the solution phase to the solid phase, and (iii) higher rate of initiation and propagation of the graft. It was also found that the percentage graft yield increases at the beginning and subsequently levels off.

The graft yield increased with increase of the Fe²⁺ concentration up to 4.0 × 10⁻⁴ M, and, beyond that, the graft yield decreased slightly (Fig. 2). A possible explanation for this observation might be the following: The ferrous ions first react

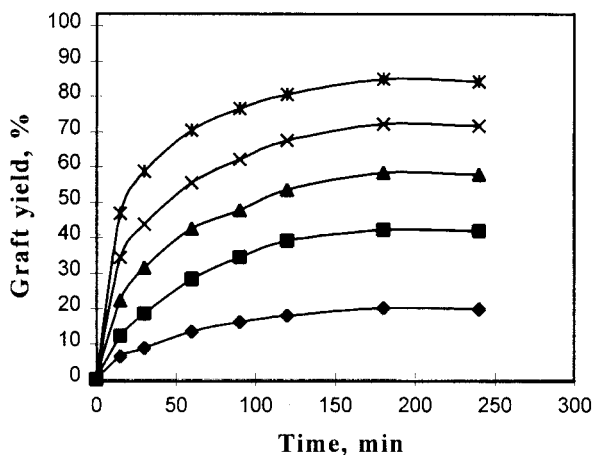


Figure 1 Effect of reaction time and temperature on graft yield: (◆) 30°C; (■) 40°C; (▲) 50°C; (X) 60°C; (*) 70°C; $[\text{FeAmSO}_4] = 4.0 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{O}_2] = 6.0 \times 10^{-3} \text{ M}$; $\text{CH} = 5 \text{ g L}^{-1}$; $\text{AA} = 25 \text{ g L}^{-1}$.

with H_2O_2 to produce ferric ions and hydroxyl radicals. The hydroxyl radicals might attack lignocellulose to produce macroradicals. The newly produced ferric ions then react with the phenolic hydroxyl group of the lignin to produce phenolic radicals and ferrous ions. These ferrous ions in the system could be used repeatedly in a way that the freshly produced ferric ions might react with phenolic hydroxyl groups of lignin to reproduce ferrous ions.⁴ Thus, only a limited concentration of Fe^{2+} ions was required to initiate the graft copolymerization. Beyond this, the con-

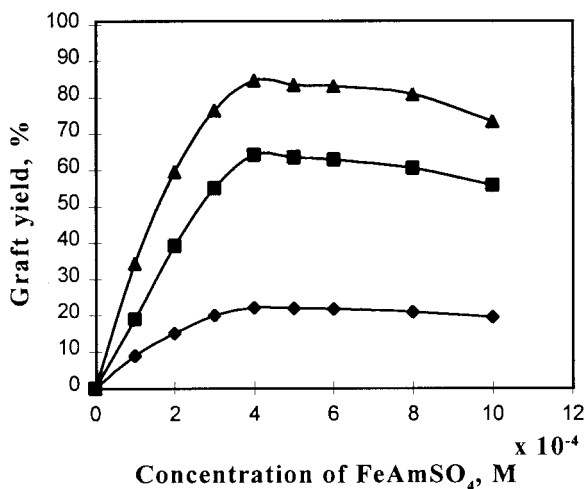


Figure 2 Effect of concentration of ferrous ammonium sulphate on graft yield: (◆) 30°C; (■) 50°C; (▲) 70°C; $[\text{H}_2\text{O}_2] = 6.0 \times 10^{-3} \text{ M}$; $\text{CH} = 5 \text{ g L}^{-1}$; $\text{AA} = 25 \text{ g L}^{-1}$; reaction time 4 h.

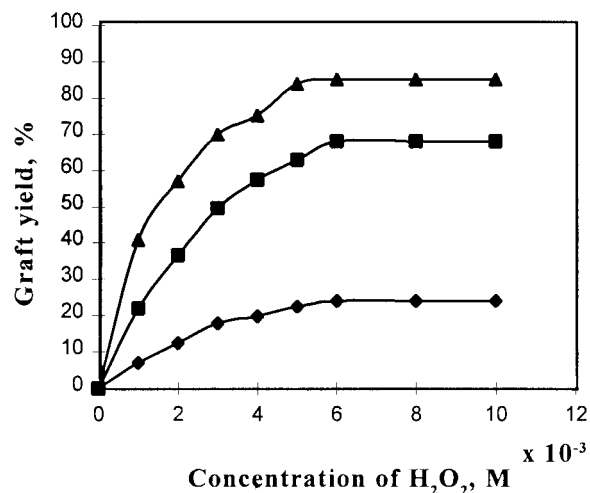


Figure 3 Effect of concentration of H_2O_2 on graft yield: (◆) 30°C; (■) 50°C; (▲) 70°C; $[\text{FeAmSO}_4] = 4.0 \times 10^{-4} \text{ M}$; $\text{CH} = 5 \text{ g L}^{-1}$; $\text{AA} = 25 \text{ g L}^{-1}$; reaction time 4 h.

centration of the initiating free radical may also decrease due to the mutual combination.

The effect of H_2O_2 concentration on the graft yield is shown in Figure 3. The graft yield increases steadily up to a $6.0 \times 10^{-3} \text{ M}$ concentration of H_2O_2 and thereafter assumes nearly constant values. This may be due to the enhanced rate of termination which balances the rate of propagation.⁸ The graft yield increased with increase of the monomer concentration as shown in Figure 4. The enhancement of grafting by increasing the monomer concentration could be associ-

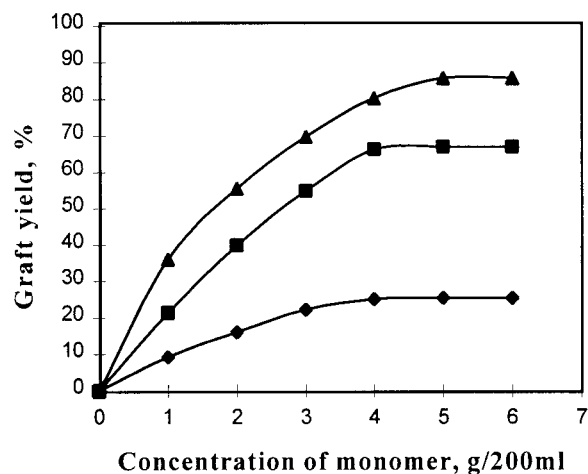
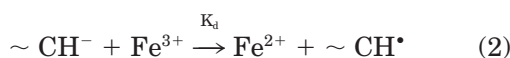
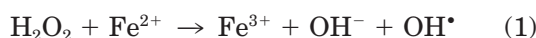


Figure 4 Effect of monomer concentration on graft yield: (◆) 30°C; (■) 50°C; (▲) 70°C; $[\text{FeAmSO}_4] = 4.0 \times 10^{-4} \text{ M}$; $[\text{H}_2\text{O}_2] = 6.0 \times 10^{-3} \text{ M}$; $\text{CH} = 5 \text{ g L}^{-1}$; reaction time 4 h.

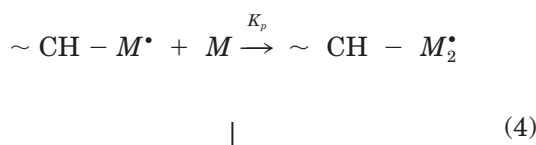
ated with the gel effect,⁹ resulting from an enhanced solubility of polyacrylamide in its own monomer. This would, consequently, increase the viscosity of the reaction medium and a reduced rate of terminations by the coupling of the growing polymer chains. Based on the above results, the medium of graft polymerization of CH is proposed as follows:

Initiation

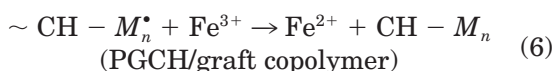
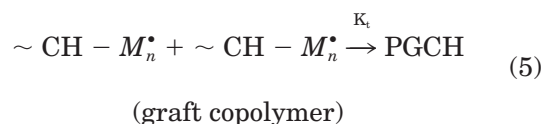


where $\sim \text{CH}^-$ is the phenolate ion of the lignin, $\sim \text{CH}^\bullet$ is the phenolic radical, and M is the monomer.

Propagation



Termination



Adsorption and Regeneration Studies

The effect of pH on the removal of Hg(II) ions by adsorption on PGCH—COOH is shown in Figure 5. The percentage adsorption of Hg(II) increased with increase in the pH up to a certain value and then decreased with further increase of the pH. The maximum adsorption of 99.4% (62.13 μmol

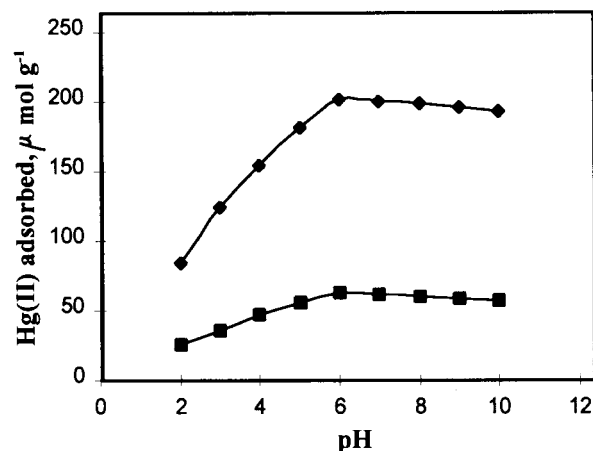
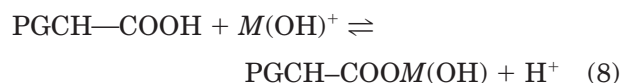
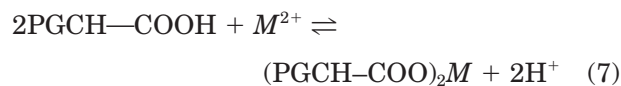


Figure 5 Effect of pH on Hg(II) removal by PGCH—COOH at two different initial concentrations: (■) 125 $\mu\text{mol L}^{-1}$; (◆) 500 $\mu\text{mol L}^{-1}$; reaction time 5 h; adsorbent dose 2 g L^{-1} ; ionic strength = 0.01M.

g^{-1}) and 80.7% (201.75 $\mu\text{mol g}^{-1}$) took place at pH 6.0 from the initial concentration of 125 and 500 $\mu\text{mol L}^{-1}$, respectively. It was shown that the final pH is always less than the initial pH. This indicates that as the metal ions are bound on the adsorbent H^+ ions are released from the —COOH functional group into the solution and leads to the conclusion that PGCH—COOH probably acts as an acid-form ion-exchanger. In acidic pH, H^+ ions from the peripheral —COOH group can be exchanged for the Hg(II) species [Hg^{2+} and $\text{Hg}(\text{OH})^+$]. The pH_{zpc} of PGCH—COOH was found to be 5.5, and below this pH, the surface charge of the adsorbent is positive. The uptake of metal ions in the pH range 2.0–5.5 is a $\text{H}^+ - \text{M}^{2+} / \text{M}(\text{OH})^+$ exchange process:



At very low pH, the competition between Hg^{2+} and the higher concentration of H^+ ions for sorption sites is in favor of H^+ , and, as a result, less removal efficiency was observed at low pH. With increase of the pH, the enhancement of adsorption is apparently due to the hydrolysis of the exchanging cations, since the hydroxy complex, that is, $\text{Hg}(\text{OH})^+$, is sorbed in preference to the uncomplexed cations²³ (Hg^{2+}). However, the sites responsible for the sorption process are not exclu-

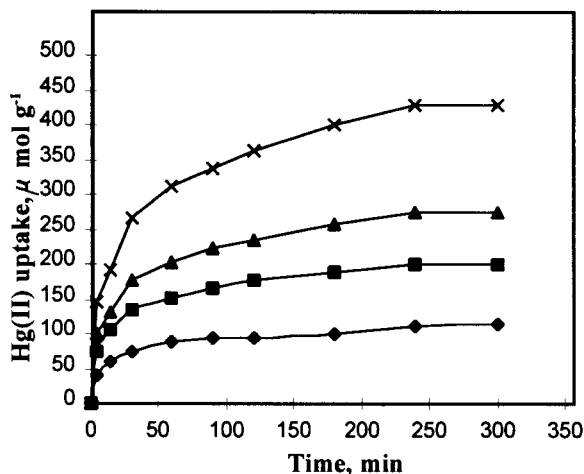


Figure 6 Effect of contact time and initial concentration on Hg(II) adsorption by PGCH—COOH: (◆) 250 $\mu\text{mol L}^{-1}$; (■) 500 $\mu\text{mol L}^{-1}$; (▲) 750 $\mu\text{mol L}^{-1}$; (x) 1250 $\mu\text{mol L}^{-1}$; pH 6.0; adsorbent dose = 2 g L^{-1} ; ionic strength = 0.01M.

sively due to the —COOH groups. Other sites on the PGCH—COOH can also contribute to the adsorption process. In acidic medium, the electromeric effect of amide groups in PGCH—COOH leads to surface protonation and possesses a net positive charge on the surface.²⁴ These H^+ ions from the surface are also exchanged with positively charged sorbate species and are subsequently coordinated with the amide groups. Similar results are reported for the amide groups contained in the divinylbenzene-crosslinked polyacrylamide resins for the coordination of metal ions.²⁵ Decrease in the sorption at higher pH is due to the formation of soluble hydroxy complexes.

The adsorption data for the uptake of Hg(II) ions versus contact time for a fixed adsorbent dose (2 g/L) with four different initial concentrations are presented graphically in Figure 6. These plots indicate that the remaining concentration of metal ions becomes asymptotic to the time axis representing nearly an equilibrium time. The equilibrium was attained after 4 h and was independent of initial Hg(II) concentrations. Therefore, 5 h was taken as the optimum equilibration period for all the other experiments. With change in the concentration of the solution from 250 to 1250 $\mu\text{mol L}^{-1}$, the percentage adsorption of Hg(II) decreased from 90% (112.2 $\mu\text{mol g}^{-1}$) to 68% (426.6 $\mu\text{mol g}^{-1}$). It can be concluded that high removal at low concentration is important in terms of industrial application.

Adsorption kinetics was extensively studied: In this work, the model chosen refers to the theory

developed by Urano and Tachikawa.²⁶ In this model, external diffusion is considered as negligible, relative to the low overall sorption rate. The sorption kinetics are modeled according to the following equation:

$$f(Q_t/Q_e) = -\log[1 - (Q_t/Q_e)^2] = \frac{\pi^2 D t}{2.3 r^2} \quad (9)$$

where Q_t and Q_e are the sorbate concentration in the solid at time t and at equilibrium ($t \rightarrow \infty$); r , the particle radius; and D , the diffusion coefficient in the solid ($\text{m}^2 \text{s}^{-1}$). Plots of $f(Q_t/Q_e)$ versus t at different temperatures (Fig. 7) are straight lines passing through the origin. It indicates the validity of the Urano and Tachikawa equation developed for the particle diffusion-controlled kinetics. The increase in the slope of the straight-line plots, and, hence, in the rate of exchange with increase in the temperature, suggests that the rate of exchange is governed by the diffusion of exchanging ions within the exchanger particles. The values of the diffusion coefficient, D , at different temperatures calculated from the slope and adsorbent radius are shown in Table I.

The linear relationship between $\log D$ and $1/T$ (regression analysis) enables the calculation of the energy of activation (E_a) for the self-diffusion of Hg(II) and pre-exponential constant D_0 using the Arrhenius equation:

$$D = D_0 \exp(-E_a/RT) \quad (10)$$

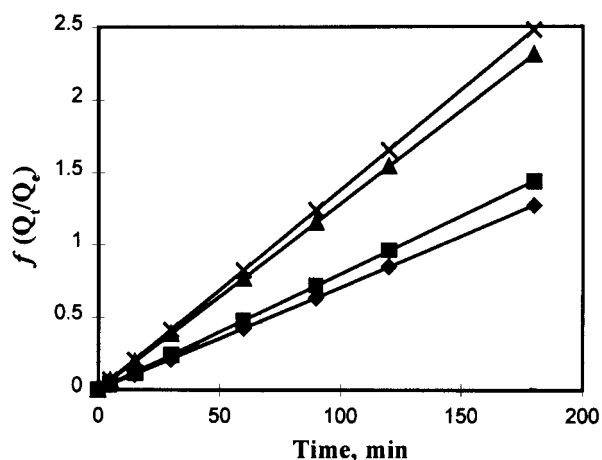


Figure 7 Plots of $f(Q_t/Q_e)$ versus time for the Hg(II) removal by PGCH—COOH: (◆) 30°C; (■) 40°C; (▲) 50°C; (x) 60°C; pH 6.0; adsorbent dose = 2 g L^{-1} ; ionic strength = 0.01M.

Table I Langmuir Parameters and Diffusion Coefficients for the Sorption of Hg(II) onto PGCH—COOH

Temperature (°C)	Langmuir Parameters		
	Q_{\max} (mol g ⁻¹)	K (L mol ⁻¹)	Diffusion Coefficient (m ² S ⁻¹)
30	6.22×10^{-4}	4.69×10^3	3.81×10^{-12}
40	6.64×10^{-4}	5.52×10^3	4.30×10^{-12}
50	6.77×10^{-4}	7.93×10^3	6.91×10^{-12}
60	6.96×10^{-4}	9.92×10^3	7.42×10^{-12}

The value of E_a is calculated from the slope of log D versus $1/T$ plot (not shown) using regression analysis and is equal to 20.76 kJ mol⁻¹. The relatively low value of E_a suggests that Hg(II) sorption is a diffusion-controlled process.²⁷ The value of D_0 is calculated from the intercept of the plot, and substitution in the following equation gives the entropy of activation (ΔS^*):

$$D_0 = 2.73 d^2 kT/h \exp(\Delta S^*/R) \quad (11)$$

where d is the distance between the adjacent exchanging sites in the exchanger²⁸ which is assumed to be equal to 5×10^{-8} cm; k , the Boltzmann constant; h , Planck's constant; and R , the gas constant and T is taken as 273 K. The negative value of ΔS^* (-123.35 J K⁻¹ mol⁻¹) indicates a greater order of reaction during the adsorption of Hg(II) ions onto PGCH—COOH and also reflects the affinity of the adsorbent material for Hg(II) ions.

The adsorption data of Hg(II) ions by PGCH—COOH was analyzed using the Langmuir model to evaluate the mechanistic parameters associated with the adsorption process. The linear form of the Langmuir isotherm equation is represented by the following equation:

$$\frac{1}{Q_e} = \frac{1}{C_e K Q_{\max}} + \frac{1}{Q_{\max}} \quad (12)$$

where Q_e is the equilibrium amount adsorbed (mol g⁻¹); C_e , the equilibrium concentration of the adsorbate (mol L⁻¹); and Q_{\max} and K , Langmuir constants related to the maximum adsorption capacity and equilibrium constant or binding energy, respectively. The straight-line plots of $1/Q_e$ versus $1/C_e$ at different temperatures (Fig. 8) show the validity of the Langmuir isotherm model, consequently suggesting the formation of monolayer coverage of the adsorbate on sorbent

surface. The Langmuir parameters Q_{\max} and K calculated from the slope and intercept of the plots are shown in Table I. Although direct comparison of PGCH—COOH with other adsorbent materials having different chelating groups is difficult, owing to the different experimental conditions, it was found, in general, that the adsorption capacity (Q_{\max}) of PGCH—COOH for Hg(II), determined to be 6.22×10^{-4} mol g⁻¹, is higher than that of amino-functionalized chitosan²⁹ (4.00×10^{-4} mol g⁻¹), 2-mercaptobenzothiazole-treated clay³⁰ (0.14×10^{-4} mol g⁻¹), humic acid³¹ (0.50×10^{-4} mol g⁻¹), formaldehyde-polymerized sawdust³² (1.94×10^{-4} mol g⁻¹), and polyacrylamide-grafted titanium(IV) oxide gel¹³ (3.75×10^{-4} mol g⁻¹).

The presence of the side group [—CONH—(CH₂)₂—NHCO(CH₂)₂—] on PGCH—COOH can affect the adsorption reaction by its spacer effect.³³ To examine the spacer effect of the side

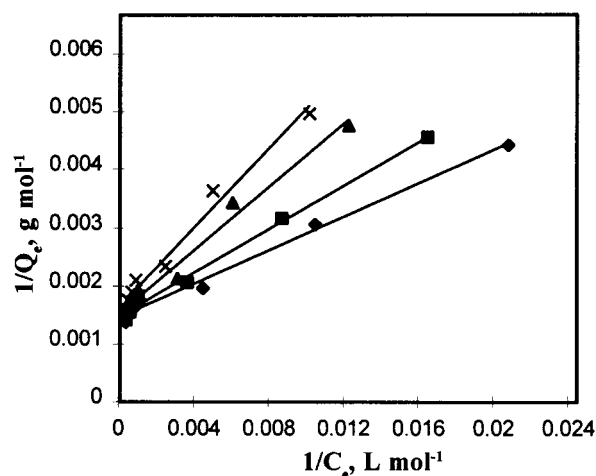


Figure 8 Langmuir plots for the adsorption of Hg(II) on PGCH—COOH: (x) 30°C; (▲) 40°C; (■) 50°C; (◆) 60°C; pH 6.0; adsorbent dose = 2 g L⁻¹; ionic strength = 0.01M.

Table II Equilibrium Parameter for the Sorption of Hg(II) onto PGCH—COOH

Initial Concentration ($\mu\text{mol L}^{-1}$)	R_L Values			
	30°C	40°C	50°C	60°C
500	0.30	0.27	0.20	0.17
750	0.22	0.20	0.14	0.12
1250	0.15	0.13	0.09	0.07
2000	0.10	0.08	0.06	0.05
2500	0.08	0.07	0.05	0.04
3000	0.07	0.06	0.04	0.03
3750	0.05	0.05	0.03	0.02

group in PGCH—COOH on Hg(II) adsorption, the values of the Langmuir parameters obtained for Hg(II) adsorption on PGCH—COOH were compared with those obtained for an adsorbent having the —COOH functional group but without any other side group. For this, we prepared an adsorbent from CH by grafting acrylic acid using the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ redox initiator. This adsorbent material has the —COOH functional group but does not contain any side group. Adsorption isotherm experiments were carried out at different initial concentrations of Hg(II) ions at pH 6.0 and 30°C (article under preparation). The values of the Langmuir parameters, Q_{max} and K , were calculated using linear regression analysis and found to be $5.12 \times 10^{-4} \text{ mol g}^{-1}$ and $3.34 \times 10^3 \text{ L mol}^{-1}$, respectively. The higher values of Q_{max} ($6.22 \times 10^{-4} \text{ mol g}^{-1}$) and K ($4.69 \times 10^3 \text{ L mol}^{-1}$) observed for PGCH—COOH may be due to the spacer effect of the side group [—CONH—(CH₂)₂—NHCO(CH₂)₂—] which is absent in acrylic acid-polymerized CH. This side group in PGCH—COOH acts as a handle so that the —COOH group is made to protrude into the homogeneous medium. Many researchers have also reported the same spacer effect of the side group present in the carboxylic acid-functionalized synthetic polymers for their unusual binding capacities toward metal ions³³.

Table III Desorption and Regeneration Data

No. Cycles	Adsorption ($\mu\text{mol g}^{-1}$)	Recovery (%)
1	62.03	98.2
2	60.03	96.7
3	57.29	93.9
4	52.69	91.4

The essential characteristics of Langmuir isotherms have been described by the equilibrium parameter³⁴ R_L which is equal to $1/(1 + KC_0)$, where K is the Langmuir constant, and C_0 , the initial concentration. The values of R_L in the present investigation (Table II) were found to be in the range $0 < R_L < 1$, showing favorable adsorption.

With a view to remove the adsorbed metal ions and recycled adsorbent, the use of HCl as an eluent was examined. Table III summarizes the desorption and regeneration data. After three cycles, the adsorption capacity of PGCH—COOH declined from 62.03 to 52.69 $\mu\text{mol g}^{-1}$, whereas the recovery of Hg(II) with 0.2M HCl decreased from 98.2% in the first cycle to 91.4% in the fourth cycle. About a 3–5% sorbent weight loss was observed after HCl treatment. The higher percentage desorption at low pH may be due to the presence of a large concentration of H^+ ions which release the Hg(II) ions from the sorbent surface to the solution. The results show that the spent adsorbent can be readily regenerated for repeated use with very little loss of weight of the adsorbent material.

The suitability of the adsorbent material for treating Hg(II) wastewater was tested using synthetic and industrial wastewaters. Industrial wastewater collected from a chloralkali industry situated in Cochin City (India) was characterized using standard methods. The composition of both the synthetic and industrial wastewaters is given in Table IV. The amount of Hg(II) in the industrial wastewater was found to be very low ($17.0 \mu\text{mol L}^{-1}$) and, hence, it was spiked with a Hg(II) solution so that the final concentration of Hg(II)

Table IV Composition of Synthetic and Industrial Wastewaters

	Composition ($\mu\text{mol L}^{-1}$)
Synthetic wastewater	Hg: 125; Mg: 1029; Ca: 1000; Na: 1087; K: 1024; NH ₄ : 1111; SO ₄ : 1042; H ₂ PO ₄ : 515; Cl: 2817; CH ₃ COO: 1017
Industrial wastewater	Hg: 17.0; Pb: 15.0; Cd: 2.7; Mg: 843.6; Ca: 1002.5; NH ₄ : 1555.5; Na: 11474.0; H ₂ PO ₄ : 115.4; NO ₃ : 230.6; Cl: 9850.7; BOD: 1865.6; COD: 4571.9 (SS: 317.5 mg L ⁻¹)

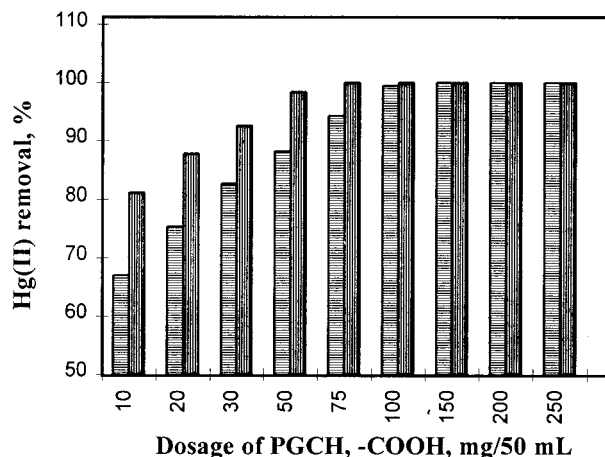


Figure 9 Effect of adsorbent dose for the removal of Hg(II) from wastewater by PGCH—COOH: (▨) synthetic wastewater; (▩) industrial wastewater; pH 6.0; agitation time = 5 h.

was $50.0 \mu\text{mol L}^{-1}$. The effect of the adsorbent dose on Hg(II) removal by PGCH—COOH from the wastewater is given in Figure 9. The results reveal that the capacity of PGCH—COOH for the removal of Hg(II) was not affected in the presence of other ions. Complete removal of Hg(II) from 50 mL of the synthetic and industrial wastewaters occurred at 150 and 75 mg of the adsorbent dose, respectively, which are in good agreement with those obtained from the batch experiments mentioned above. From the above observations, it may be concluded that PGCH—COOH, which was prepared by copolymerization, can be successfully used as an adsorbent for the treatment of Hg(II)-rich water and wastewater.

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