

Mercury(II) removal from aqueous solutions and wastewaters using a novel cation exchanger derived from coconut coir pith and its recovery

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Abstract

A new adsorbent (PGCP-COOH) having carboxylate functional group at the chain end was synthesized by grafting poly(hydroxyethylmethacrylate) onto coconut coir pith, CP (a coir industry-based lignocellulosic residue), using potassium peroxydisulphate as an initiator and in the presence of *N,N*-methylenebisacrylamide as a cross-linking agent. The adsorbent was characterized with the help of infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy, and potentiometric titrations. The ability of PGCP-COOH to remove Hg(II) from aqueous solutions was assessed using batch adsorption technique under kinetic and equilibrium conditions. Adsorbent exhibits very high adsorption potential for Hg(II) and more than 99.0% removal was achieved in the pH range 5.5–8.0. Adsorption process was found to follow first-order-reversible kinetics. An increase of ionic strength of the medium caused a decrease in metal removal, indicating the occurrence of outer-sphere surface complex mechanism. The equilibrium data were fitted well by the Freundlich isotherm model ($R^2 = 0.99$; $\chi^2 = 1.81$). The removal efficiency was tested using chlor-alkali industry wastewater. Adsorption isotherm experiments were also conducted for comparison using a commercial carboxylate-functionalized ion exchanger, Ceralite IRC-50. Regeneration experiments were tried for four cycles and results indicate a capacity loss of <9.0%.

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1. Introduction

Treatment of contaminated water to remove soluble heavy metals has been and continues to be a technical challenge due to very low concentrations established by current regulations. Mercury, which is widely used and extremely toxic in relatively low dosages is one of the principle heavy metals responsible for causing neurological and renal disturbances as it can easily pass through blood–brain barrier and affect the foetal brain. The main anthropogenic path way through which Hg(II) enters the water bodies is via wastes from industrial processes such as chlor-alkali, paper and pulp, oil refinery, mining, electroplating, paint, pharmaceutical and battery manufacturing. Among several chemical and physical methods, adsorption process is one of the effective techniques that has been successfully employed for metal removal from wastewater. A wide range of adsorbents has

been used for removing Hg(II) from wastewaters and has been reviewed by Krishnan and Anirudhan [1]. Several recent publications utilized inexpensive naturally occurring lignocellulosic materials, e.g. wheat straw, peanut shell, moss peat, bagasse fly ash, tree fern, gram husk, coconut coir pith and saw dust for heavy metal removal [2–5]. These materials were found to have good adsorption capacity due to substances inherently associated with cellulose such as lignin, tannin and pectin, which contains polyphenolic and aliphatic hydroxyl and carboxylic groups. The main disadvantages of these materials are their low resistance to abrasive forces in batch or column applications and leaching of some organics (water extractives) during adsorption. Many chemical modifications have therefore being thought of to improve the physical and chemical properties and also to increase the adsorption potential, which include esterification, graft copolymerization, cross-linking and quarternisation. Incorporation of different functional groups onto chemically modified lignocellulosic materials such as peanut shell, orange residue, sawdust and banana stalk has already been reported [6–10].

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Coconut coir pith (CP) is widely available and abundant natural material, which basically contains cellulose and lignin. India is the market leader in the production of coconut fruit, producing 7.5 million tonnes of CP annually. After the separation of the fiber from the coconut husk, the CP has no use and is recognized as waste in the agricultural or industrial sector. Any attempt to reutilize the CP will be worthwhile. Efforts have already been made to recycle this solid waste by using it as precursors for the preparation of potential adsorbents in water purification [11,12]. In these earlier studies, anion exchangers with different functionalities were prepared from CP, which effectively, and inexpensively decontaminates wastewater rich in heavy metals. In this study, a new adsorbent namely poly(hydroxyethylmethacrylate) grafted CP with carboxylate functionality was developed for the removal of Hg(II) from water and wastewater. The adsorption of Hg(II) onto modified CP was studied in batch system with respect to the initial pH, contact time, initial Hg(II) concentration, ionic strength, adsorbent dose and temperature.

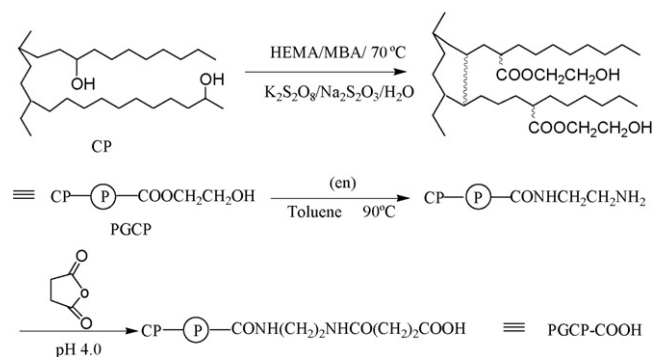
2. Experimental

2.1. Materials

All chemicals employed in this work were of pure analytical grade and the solutions were prepared with distilled water. The CP, collected from a local industry, was washed several times with distilled water to remove dirt and water-soluble and oven dried at 80 °C for 24 h. Hg(II) solutions were prepared by diluting 1000 mg/l of stock solutions of Hg(II) obtained by dissolving anhydrous HgCl₂ (Fluka, Switzerland) in distilled water. The monomer, 2-hydroxyethylmethacrylate (HEMA) was obtained from Fluka (Switzerland), distilled under reduced pressure in the presence of hydroquinone and stored at 4 °C. *N,N'*-methylenebisacrylamide (MBA) and potassium peroxydisulphate were supplied by Sigma (USA) and E-Merck, India limited, respectively and used without further purification. The particle size of the adsorbent was between 80 and 230 US standard mesh (average particle size 0.096 mm). Industrial wastewater sample was collected from chlor-alkali plant situated in Kochi (India) and was characterized by standard methods [13].

2.2. Adsorbent preparation

Scheme 1 represents the general procedure adopted for the preparation of poly(HEMA) grafted CP (PGCP) having –COOH group (PGCP-COOH). About 10 g of CP was immersed in 200 ml distilled water in a 1 l three-neck flask, which was equipped with mechanical stirrer and thermometer. About 2 g of MBA and 1 g of K₂S₂O₈ followed by 0.2 g Na₂S₂O₃ were added to the flask and was stirred for 5 min. Purified N₂ was passed through the vessel for 10 min. To the mixture 15 g of HEMA was added and stirred vigorously at 70 °C in a water bath until a solid mass was obtained. The whole sample was extracted with water in a Soxhelt for 5 h in order to remove the homopolymer formed during the grafting reaction and PGCP was collected. Grafting yield was calculated by the percentage increase in the weight as:



Scheme 1. Preparation of PGCP-COOH.

grafting yield (%) = $(W_g - W_0)100/W_0$, where W_0 and W_g are the weights of the ungrafted and grafted CP, respectively, and the value was found to be 87.3%. The dried mass was refluxed with 100 ml ethylenediamine (en) continuously for 8 h. The product was separated and washed with toluene and dried. One part by weight of the above material was refluxed at 90 °C with an equal part by weight of succinic anhydride in 1,4-dioxane (100 ml) at constant pH 4.0 for about 6 h. The mixture was cooled and filtered, then successively washed with 1,4-dioxane, water and ethanol and finally air-dried. The carboxylic acid bound PGCP (PGCP-COOH) was ground and sieved between the particle size 80 and 230 mesh (average particle size 0.096 mm) using standard sieves.

2.3. Equipments and methods of characterization

The FTIR spectra of CP and PGCP-COOH with KBr pellet were obtained with Shimadzu FTIR model 1801. The XRD patterns of the adsorbents were recorded using a Siemens D 5005 X-ray unit with Ni-filtered Cu K α radiation. A scanning electron microscope (Philips XL-3CP) operated at 12 kV was used to study the surface morphology. Porosity measurements of the adsorbents were done using a 30,000 psi mercury intrusion porosimeter (Micrometrics poresizer 9310). Viladkar et al. [14] method of methylene blue (MB) adsorption was employed to measure the specific surface area of the adsorbents. A potentiometric method [15] was used to determine the pH of point of zero charge (pH_{pzc}). The cation exchange capacity (CEC) of the adsorbents was determined by NaNO₃ saturation method using column operation. A Systronic microprocessor pH meter (model 362) was used for pH measurements. A temperature controlled water bath flask shaker (Labline, India) used for shaking all the solutions. The concentration of Hg(II) in solutions was determined using a GBC Avanta A 5450 atomic absorption spectrophotometer (AAS).

2.4. Adsorption experiments

Batch experiments were carried out using 100 ml stoppered conical flasks contain 50 ml solutions of different concentrations (10–600 mg/l) and pH (2.0–8.0) with 0.1 g of PGCP-COOH. The initial pH of the solution was adjusted with 0.1 M HCl and NaOH using pH meter. The flasks were shaken at an agitation

speed of 200 rpm in a temperature controlled water bath shaker. After equilibrium, metal bound adsorbent was separated from adsorption medium and the concentration of Hg(II) ions in the aqueous phase was measured using AAS. The adsorbed Hg(II) was obtained from the difference between the initial metal concentration and final detected metal concentration. Kinetic studies were carried out at constant pH with different initial concentrations ranging between 10 and 75 mg/l. Samples were withdrawn at regular intervals to plot the amount adsorbed versus time. For isotherm experiments, Hg(II) concentration used for adsorption was ranged from 10 to 600 mg/l.

2.5. Desorption experiments

In order to test the reusability of PGCP-COOH consecutive adsorption–desorption cycles were repeated four times by using the same effective adsorbent. Desorption of Hg(II) ions was studied using 0.1 M HCl solution. The PGCP-COOH loaded with Hg(II) was agitated with 50 ml of 0.1 M HCl. The final concentration of Hg(II) ions in aqueous solution was determined by using AAS as described above. The percentage desorption from the spent adsorbent was calculated from the amount of Hg(II) adsorbed on the PGCP-COOH and the final concentration of Hg(II) ions in the desorption medium.

2.6. Analysis of the data

All the experiments were performed in duplicate and the relative standard deviation was lower than 3.0%. When the relative error exceeded 3.0%, the data were discarded and a new experiment was conducted until the relative error falls within an acceptable range. The values of kinetic and isotherm parameters were determined by a non-linear regression analysis using ORIGIN program (version 7.5).

3. Results and discussion

3.1. Adsorbent characterization

A general scheme for the preparation of PGCP-COOH is given in Scheme 1. The PGCP was obtained through the polymerization of HEMA in the presence of MBA as cross-linking agent and CP as a support. The hydrophilic properties of the adsorbent are enhanced by MBA, while the active surface area along with the active sites is increased by CP. The methyl hydroxyl groups of the cellulose unit present in CP may be the sensitive component for polymer grafting. Thermal decomposition of persulphate initiator generates the sulphate anion radical, which reacts with hydrogen from methyl hydroxyl groups and form corresponding macroinitiator. So this system results in active centers on the substrate to radically initiate polymerization of HEMA lead to a graft copolymer. Since MBA is presented in the system, the polymer comprises a 3-dimensional cross-linked structure.

The FTIR spectra of CP and PGCP-COOH are shown in Fig. 1. The IR spectrum of CP shows an asymmetric absorption band at 3282 cm⁻¹ which is due to the hydrogen bonded O–H stretching vibrations from the cellulose structure of the CP.

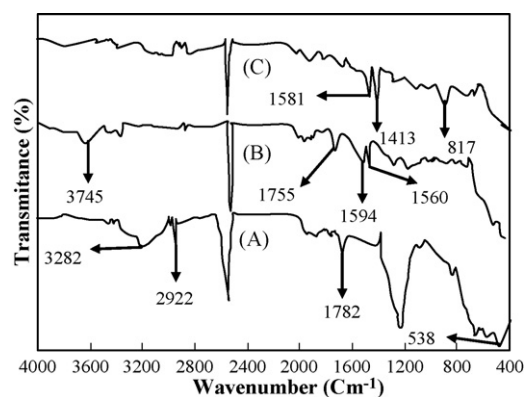


Fig. 1. FTIR spectra of CP (A), PGCP-COOH (B) and Hg(II)-PGCP-COOH (C).

The bands at 1782 and 538 cm⁻¹ for CP arise due to the C=O stretching of hemicellulose and β -glycosidic linkage. Additionally the typical absorption band at 2922 cm⁻¹ stands for the stretching vibration for C–H from –CH₂ group. The shift of stretching frequency corresponding to the presence of –OH groups in 3282 cm⁻¹ in CP to 3745 cm⁻¹ in PGCP-COOH is assigned to the involvement of hydroxyl group in the grafting of HEMA on CP. For PGCP-COOH the band at 1594 cm⁻¹ can be ascribed to the asymmetrical stretching vibration of C=O of the carboxyl group, while the band at 1755 cm⁻¹ is probably due to the stretching vibration of C=O of the –COOH group. A new characteristic band occurs at 1560 cm⁻¹, which is assigned to the N–H bending vibration of amide group on PGCP-COOH. These results clearly indicate the formation of chain (back bone) and the presence of carboxylate functional groups in PGCP-COOH.

The FTIR spectrum of Hg(II) adsorbed PGCP-COOH is also shown in Fig. 1. The spectral analysis before and after metal binding indicates that –COOH group was involved in metal adsorption. A noticeable change is that C=O vibration band at 1594 cm⁻¹ observed for the spectrum of PGCP-COOH shifted to 1581 cm⁻¹ with a different magnitude for Hg(II)-loaded PGCP-COOH. A new band appeared at 817 cm⁻¹ corresponds to Hg–O stretching vibrations. Further more the spectrum of Hg(II)-loaded PGCP-COOH displayed a peak at 1413 cm⁻¹ which can be ascribed to the symmetrical C=O stretching of the carboxyl group. These band changes indicate the carboxyl group involvement in Hg(II) adsorption probably through chelation complexation.

Fig. 2 shows SEM images for CP and PGCP-COOH particle surfaces. The surface morphology of CP is different from that of PGCP-COOH. It can be clearly observed that the CP loses its foliated surface structure and gains more homogeneous morphology. The size of the voids in original CP reduced after graft copolymerization with HEMA. The pore sizes on the CP and PGCP-COOH particles were estimated from SEM micrographs by an image analysis procedure. Fig. 2 shows that CP particles consist of irregular shape and having pore size between 5 and 20 μ m. The PGCP-COOH particles have abundant porous structure, and the size of the pores on the surface is about 4–10 μ m. Like any polymer grafted lignocellulosic materials, PGCP-COOH is also hydrophilic in nature (caused

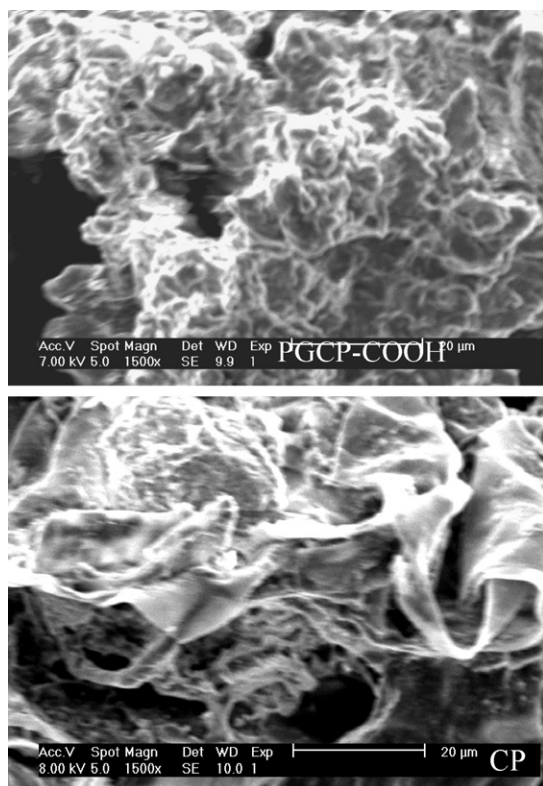


Fig. 2. SEM photographs of CP and PGCP-COOH.

by MBA cross-links) and its porous structure provides new adsorption sites from intercavities to participate in binding of metals ions.

The XRD patterns of the CP and PGCP-COOH are presented in Fig. 3. The original CP indicates the presence of a crystalline domain of cellulose structure by the appearance of peaks at

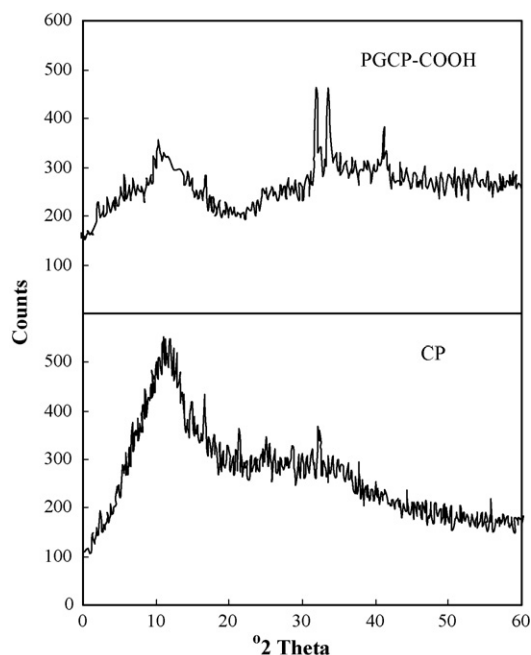


Fig. 3. XRD patterns of CP and PGCP-COOH.

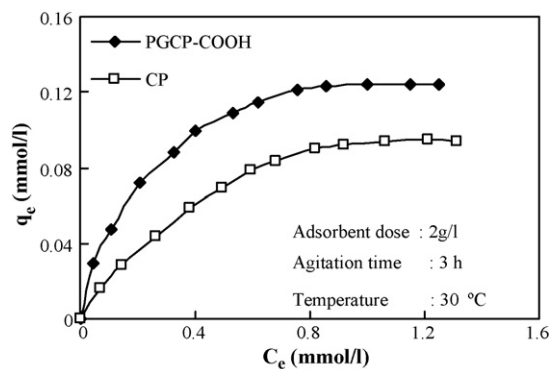


Fig. 4. Adsorption isotherm of MB onto CP and PGCP-COOH.

$2\theta = 12.3, 21.2, 41.5$ and 43.5° . This clearly suggests that cellulose molecules are arranged in ordered lattices in which $-\text{OH}$ groups are bonded by strong secondary forces. The absence of scattering angles at 12.3 and 43.5° in PGCP-COOH which is present in the original CP indicates that some rearrangement in the morphology of cellulose chain occurs as a result of chemical modification. In addition, a decrease in the intensity of the broad peak around 20° in PGCP-COOH indicating a decrease in the crystalline nature. The decrease in crystalline domains in PGCP-COOH results in the loss of tensile strength of the backbone chain and consequently enhances the mobility of the chain. It favors the protrusion of the functional groups into the aqueous medium.

The MB adsorption isotherms for CP and PGCP-COOH were obtained from batch experiments. Isotherm plots of MB onto CP and PGCP-COOH are illustrated in Fig. 4. Isotherm plots showed an initial steep slope and reached a plateau at elevated equilibrium conditions. It can be seen that the adsorption isotherms exhibit an L-type, which corresponds to the classification of Giles [16]. The L-type isotherm is based on the assumption that adsorption is a first-order chemical process and a monolayer of adsorbed material is formed onto a series of distinct sites (unsite) on the surface of the solid. The initial curvature of the plots shows that it becomes increasingly difficult for a bombarding MB molecule to find a vacant site available as more and more sites on the CP and PGCP-COOH are filled. The specific surface area (S_A) was calculated using the following equation:

$$S_A = xN_A\sigma \quad (1)$$

where x is the amount of MB adsorbed (mol/g) when surface is completely covered with a monolayer of MB. N_A is the Avogadro number and σ is the area of the adsorbent covered by one molecule of MB (130 \AA^2). Substitution of the values of x obtained from the isotherm plots in the above equation give the values of S_A . The values of x were obtained from the isotherm plots by extrapolating the ‘knee point’ to the q_e axis and taken as the point of monolayer coverage. The value of S_A was found to be higher for PGCP-COOH ($93.5 \text{ m}^2/\text{g}$) compared to that of CP ($70.2 \text{ m}^2/\text{g}$) and is probably due to the enhanced adsorption of MB in the mesopores and micropores created in PGCP-COOH, which may provide favorable adsorption sites for cations. The

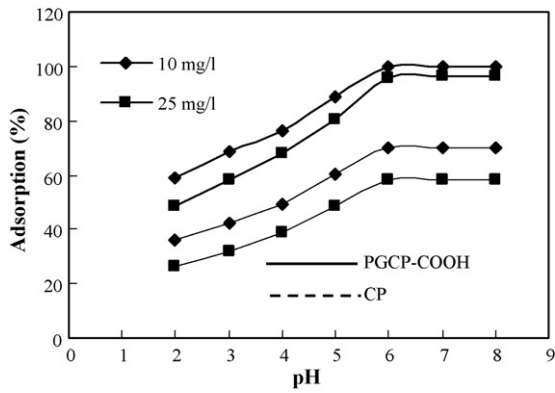


Fig. 5. The effect of pH on the adsorption of Hg(II) onto CP and PGCP-COOH.

values of pH_{pzc} of the CP and PGCP-COOH at different ionic strengths (0.001, 0.01 and 0.1 M $NaNO_3$) were determined by a potentiometric titration method [13] and were found to be 6.8 and 5.5, respectively. The decrease in pH_{pzc} after chemical modification indicates that the surface becomes more negative and this helps to adsorb metal cation through electrostatic interaction. A variation in CEC (0.42 mequiv./g for CP and 1.81 mequiv./g for PGCP-COOH) and porosity (0.32 ml/g for CP and 0.41 ml/g for PGCP-COOH) was also observed after chemical modification. The carboxyl content of PGCP-COOH was determined by neutralization of carboxyl groups of the adsorbent with 0.1 M $NaHCO_3$ solution using a titration method described by Boehm [17]. The carboxyl content of PGCP-COOH was found to be 1.94 mequiv./g.

3.2. Effect of pH on Hg(II) removal

Since the surface charge of an adsorbent could be modified by changing pH of the solution, pH is one of the most important parameters affecting the adsorption of metal ions. To study the influence of pH on the adsorption capacity of CP and PGCP-COOH for Hg(II), experiments were performed using an initial concentration of 10 and 25 mg/l over the pH range 2.0–8.0 and the results are presented in Fig. 5. The maximum adsorption percentage of Hg(II) by both adsorbents was observed at the pH range 5.5–8.0 and significantly decreased by reducing the pH values to 2.0. Higher adsorption at higher pH values may imply that metal ions interact with both types of adsorbents by a chelating mechanism. A maximum adsorption of 69.8 and 58.2% for CP and 99.8 and 96.6% for PGCP-COOH was seen at an initial concentration of 10 and 25 mg/l, respectively at pH 6.0. These results clearly show that PGCP-COOH is more effective than CP for the removal of Hg(II) from aqueous solutions. Considering that the adsorbent PGCP-COOH consists of carboxylic acid groups, which act as anionic chelating agents, the adsorption process may be attributed to the electrostatic attraction between positively charged metal ions and negatively charged sorbent. At lower pH values (<3.0), the active sites of the adsorbent are less available for Hg(II) ions due to protonation of the above sites at higher H^+ concentration. As pH increased the degree of protonation of surface gradually reduced and approached zero at pH 5.5 (pH_{pzc}) resulting in a gradual increase in the adsorp-

tion. At the pH range 3.0–5.5, it is believed that ion exchange and complexation process are major mechanisms for removal of Hg(II) ions



It is observed that as Hg(II) is adsorbed on the adsorbent from solution there is decrease in pH of the solution. When the initial pH of the reaction mixture varied between 3.0 and 6.0, the final pH of the reaction mixture remained between 2.3 and 4.9 and 2.2 and 4.2 for an initial concentration of 10 and 25 mg/l, respectively. Above pH 6.0 where Hg^{2+} and $HgOH^+$ species were present in the solution [18], the adsorbent surface began acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of Hg(II) ions. Since PGCP-COOH had higher adsorption efficiency than CP, subsequent adsorption experiments with Hg(II) were performed only on PGCP-COOH.

3.3. Effect of contact time and Hg(II) concentration

The effect of contact time on the adsorption of Hg(II) were also studied for different Hg(II) concentrations and the results are presented in Fig. 6. The initial rate was rapid and thereafter adsorption was gradual and equilibrium was reached after 3 h. It was also indicated that the extent of adsorption was highly dependent on the initial Hg(II) concentration. An increase of Hg(II) concentration accelerates the diffusion of Hg(II) from the bulk solution onto adsorbent due to the increase in the driving force of the concentration gradient. Hence the amount of Hg(II) adsorbed at equilibrium increased from 4.97 mg/g (99.8%) to 32.90 mg/g (87.7%) with an increase in initial concentration from 10 to 75 mg/l. The equilibrium time was independent of initial Hg(II) concentration. Therefore, further studies were car-

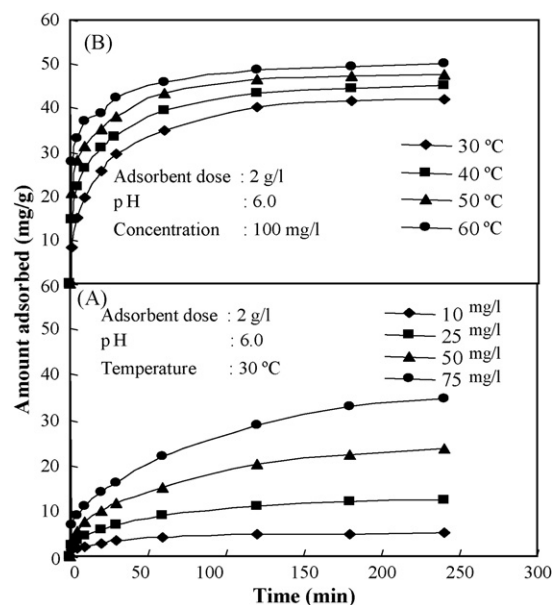


Fig. 6. The effect of contact time on the adsorption of Hg(II) onto PGCP-COOH at different (A) concentrations and (B) temperatures.

ried out using a period of 3 h as a suitable contact time for Hg(II) adsorption.

3.4. Effect of temperature

To determine the effect of temperature, adsorption studies of Hg(II) were performed at four different temperatures, i.e., 30, 40, 50 and 60 °C and the results are shown in Fig. 6. It is observed that the uptake of Hg(II) increases with increasing temperature. The increase in adsorption with increasing temperature indicates that the process of adsorption of Hg(II) is endothermic in nature.

3.5. Kinetic model

To understand the practical application of adsorption and design a sorption reactor, the kinetic data obtained in this study were treated by the first-order kinetic model cited by Lopez et al. [19]. The model is given by the following equation:

$$\ln \left(\frac{C_t}{C_0} \right) = -k \left(\frac{S_S}{V} \right) t \quad (3)$$

where C_t is the Hg(II) concentration at a time t (mg/l), C_0 the initial Hg(II) concentration (at $t=0$), k the rate constant, V the volume of the solution placed in contact with the adsorbent, and the outer surface of the adsorbent per unit volume of particle free slurry (cm^{-1}) is calculated as $S_S = 6m/[d_p \rho_p (1 - \varepsilon_p)]$, where d_p is the particle diameter (cm), ρ_p the density of the adsorbent (g/ml), ε_p the porosity of adsorbent particle (ml/g) and m is the mass of the adsorbent per unit volume (g/l). The values of k determined from the slope of the plots ($R^2 > 0.98$) corresponding to Eq. (3) were found to be 8.25×10^{-2} , 4.78×10^{-2} , 3.65×10^{-2} and 3.03×10^{-2} cm/s at an initial concentration of 10, 25, 50 and 75 mg/l, respectively at 30 °C. Since increasing the Hg(II) concentration in the solution reduced the diffusion of metal ions in the boundary layers, the k values decreased with increasing initial concentration. It is clear from the values of k that the velocity of Hg(II) transport from the bulk to the solid phase is quite rapid and this reflects the efficiency of PGCP-COOH for the treatment of wastewater rich in Hg(II) ions. The values of k at 30, 40, 50 and 60 °C were also calculated and were found to be 2.26×10^{-2} , 2.53×10^{-2} , 3.95×10^{-2} and 4.54×10^{-2} cm/s, respectively for an initial concentration of 100 mg/l. The increase in temperature favors the adsorption process by activating the adsorption sites or the increase in desolvation of adsorbing species as the desolvation is an endothermic process. This may also be explained by the thermal motion of adsorbed species being one of the significant factors in the process of adsorption from solution. An Arrhenius plot ($\ln k$ vs. $1/T$) was carried out on the data and from the slope, the activation energy for the process was calculated to be 21.28 kJ/mol, indicating that intraparticle diffusion might have been the essential rate-limiting step in the adsorption process [20].

3.6. Effect of ionic strength

The ionic strength of aqueous solution is an important variable that influences the absorption of anions and cations at the solid–liquid interfaces. The effect of ionic strength on Hg(II)

adsorption was studied by conducting batch experiments at varying concentration of NaCl solutions. As was expected the adsorbed amount decreases as the ionic strength increases, due to the involvement of electrostatic attraction between the adsorbent and adsorbate [21]. The adsorption capacity with NaCl concentration of 0.001, 0.005, 0.01, 0.05, and 0.1 M was found to be 83.2, 75.6, 70.1, 63.3 and 59.8%, respectively at an initial concentration of 25 mg/l. Earlier workers explain that the reduction of metal removal percentage is due to the increase of NaCl and thus by the presence of competing Na^+ ions for metal binding [22]. McBride [23] indicates that ions that form outer-sphere surface complexes show decrease in adsorption with increase in ionic strength. Ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with increasing ionic strength. Thus in the case of Hg(II) adsorption by PGCP-COOH these two phenomena, Na^+ ions competition and outer-sphere surface complex formation could be considered to describe the decrease of Hg(II) adsorption.

3.7. Adsorption isotherm

Equilibrium isotherm was measured to determine the capacity of PGCP-COOH for Hg(II) ions. Adsorption isotherm of Hg(II) ions onto PGCP-COOH at 30 °C is shown in Fig. 7. The Hg(II) uptake increased with increase in equilibrium concentrations. According to Giles classification [16], the adsorption isotherm for 30 °C belongs to H-type, subgroup 2, which indicates that PGCP-COOH has a high affinity for Hg(II) ions, i.e., it is strongly adsorbed on the adsorbent and that there is no competition from the solvent for adsorption sites. It also indicates that the adsorption of Hg(II) is enhanced at higher concentrations. At very low concentrations, in practice the PGCP-COOH adsorbs the entire quantity of the Hg(II) ions, or at least there is no measurable amount remaining in solution. The isotherm data were fitted with the Freundlich isotherm model. In Fig. 7, the adsorption isotherm was approximated by the non-linear Freundlich isotherm model: $q_e = K_F C_e^{1/n}$, where q_e is the observed adsorption capacity (mg/g) and C_e is the equilibrium concentration (mg/l), K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption inten-

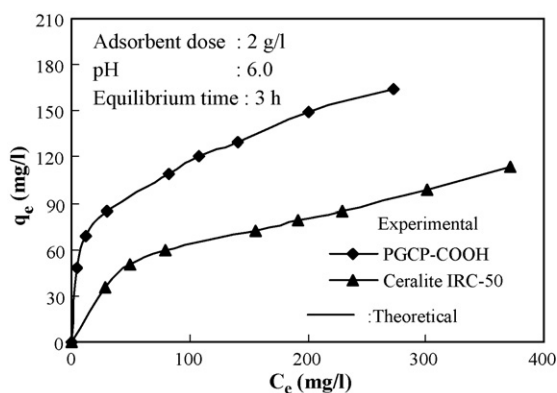


Fig. 7. Comparison of the experimental and model fits of the Freundlich isotherm (line) for the adsorption of Hg(II) onto PGCP-COOH and Ceralite IRC-50 at 30 °C.

sity, respectively. The values of K_F and $1/n$ were determined by a non-linear regression analysis using ORIGIN program (version 7.5) and were found to be 13.73 and 0.451, respectively. From the correlation coefficient ($R^2 = 0.99$) and χ^2 -value (1.81), the Freundlich model adequately describes the adsorption isotherm data. The ultimate adsorption capacity of the adsorbent can be calculated from the isothermal data by substituting the required equilibrium concentration in the Freundlich equation. Thus for an equilibrium concentration of 1.0 mg/l, each gram of PGCP-COOH can remove 13.73 mg of Hg(II) at 30 °C.

3.8. Comparison with commercial ion exchanger

Adsorption isotherm experiments were also performed using a commercial carboxylic acid functionalized cation exchanger, Ceralite IRC-50 obtained from M/S Loba Chemie Mumbai, India. The equilibrium data so obtained were converted to Freundlich isotherm as shown in Fig. 7. Isotherm parameters were obtained using non-linear regression analysis. The higher value of R^2 (0.99) and lower value of χ^2 (1.52) obtained for Freundlich model indicate that this model could define the experimental results in the Ceralite IRC-50–Hg(II) system. The calculated values of K_F and $1/n$ were 8.44 and 0.422, respectively, which were lower than those calculated for PGCP-COOH.

3.9. Application of the adsorbent

The developed PGCP-COOH system was tested in the laboratory to remove Hg(II) from a Chlor-alkali industry wastewater sample. The characterization of water sample was done using standard methods [13]. The sample contained apart from Hg (29.3 mg/l) other metal ions based on Pb^{2+} (2.9 mg/l), Cd^{2+} (0.6 mg/l), Mg^{2+} (33.3 mg/l), Ca^{2+} (27.7 mg/l), and Na^+ (311.2 mg/l) as well as anions like SO_4^{2-} (12.3 mg/l), NO_3^- (30.2 mg/l), NO_2^- (1.7 mg/l) and Cl^- (460.4 mg/l). The effect of adsorbent dose on Hg(II) removal from wastewater was investigated. These results are presented in Fig. 8. It can be seen that the percentage Hg(II) adsorption increases from 62.3% (31.15 mg/g) to 99.9% (4.99 mg/g) with increasing PGCP-COOH dosage from 0.5 to 5.0 g/l. However, unit adsorption or adsorption per unit mass of adsorbent decreases and the effect is

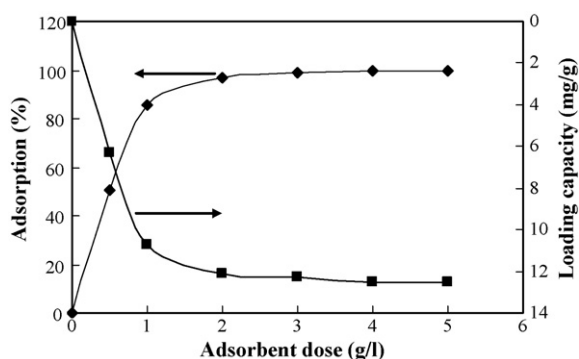


Fig. 8. The effect of adsorbent dose on the adsorption of Hg(II) from chlor-alkali industry wastewater by PGCP-COOH.

more pronounced at higher adsorbent dosages. This is because, as the dose of adsorbent is increased, there is less commensurate increase in adsorption resulting from the lower utilization of the adsorption capacity of the adsorbent. The particle interaction brought about by high dosages may also desorb some of the Hg(II) ions, which are only loosely and reversibly bound to the adsorbent surface. It is found that an adsorbent dosage of 4.0 g/l is sufficient to reach the WHO standard of ≈ 0.01 mg/l, indicating that PGCP-COOH has greater ability to remove Hg(II) from wastewater. The possible release of any organics into the solution during Hg(II) adsorption by PGCP-COOH is also investigated. For this, the amount of chemical oxygen demand (COD) in water sample, before and after adsorption was determined by means of dichromate method [13]. Following the increase in the concentration of lignocellulosic-based adsorbents in wastewater, COD in water also expected to increase after adsorption. Fortunately, even when the quantity of PGCP-COOH increased from 0.5 to 5.0 g/l the amount of COD increased from 76.3 to 94.6 mg/l in the treated water samples and these values are lower than that of initial amount present in water sample (126.5 mg/l). Graft copolymerization induces a stabilization of the hydrolysable compounds of CP by creating new bonds on constitutive units and makes the CP able to adsorb Hg(II) ions without releasing any organic substances.

3.10. Reusability

To be useful in Hg(II) recycling process, adsorbed Hg(II) should be easily desorbed without destroying the adsorbent material under the suitable conditions. Since ion exchange is generally reversible, the Hg(II) desorption performance was examined using HCl solution. It was found that Hg(II) desorption was 47.7, 73.8, 92.3, 97.7 and 98.3% with 0.005, 0.01, 0.05, 0.1 and 0.2 M HCl, respectively. The highest desorption percentage was obtained when the highest tested HCl concentration, probably due to the formation of chloro-complexes with metal ions. To test the suitability and stability of the adsorbent it was subjected to successive adsorption and desorption cycles with 0.2 M HCl as the desorbing agent and the results are shown in Fig. 9. After four cycles the adsorption capacity of PGCP-COOH decreased from 99.3 to 90.4% while the

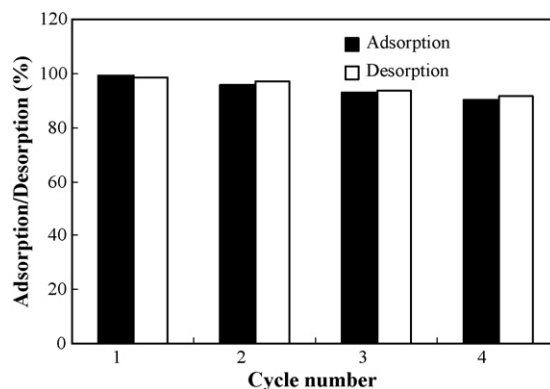


Fig. 9. Four cycles of Hg(II) adsorption–desorption with 0.2M HCl as the desorbing agent.

recovery of Hg(II) decreased from 98.7% in the first cycle to 91.4% in the fourth cycle. At the end of four cycles, the recovery and removal were little decreased. These results indicate that the Hg(II) adsorption on the PGCP-COOH is not completely reversible and the bonding between PGCP-COOH and some of the adsorbed Hg(II) ions is likely strong and, as a result, sorption capacity is reduced in the subsequent cycles.

4. Conclusions

In this study, the ability of poly(hydroxyethylmethacrylate)-grafted coir pith having carboxylate functional group (PGCP-COOH) to bind Hg(II) ions from water and wastewater was investigated by batch technique. Hg(II) removal was efficiently performed in the initial pH range of 5.5–8.0, but efficiency decreased with the decrease of pH. The equilibrium time was reached within 3 h. The adsorption follows a first-order rate reaction with lower concentration and high temperature being favored for an efficient removal from aqueous solution. The equilibrium isotherm data were fitted well by Freundlich isotherm as evidenced from the good agreement between the experimental and calculated values. A wastewater sample containing Hg(II) obtained from chlor-alkali industry showed satisfactory removal of Hg(II). The adsorbed Hg(II) desorbed quantitatively by 0.2 M HCl solution and the adsorbent can be reused for three cycles consecutively. The results of the present investigations illustrate that PGCP-COOH could be used as an adsorbent for the effective removal of Hg(II) from aqueous solutions and other industrial effluents, further work should be carried out to optimize the system from the regeneration point of view and also to better characterize the adsorption behavior of the adsorbent with respect to column operation.

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