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Adsorption Characteristics of Cadmium(II) onto Functionalized Poly(hydroxyethylmethacrylate)-Grafted Coconut Coir Pith

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Abstract This study explored the feasibility of utilizing a novel adsorbent, poly(hydroxyethylmethacrylate)-grafted coconut coir pith with carboxyl functionality (PGCP-COOH) for the removal of cadmium(II) from water and wastewater. Maximum removal of 99.9% was observed for an initial concentration of 25 mg/L at pH 6.0 and adsorbent dose of 2.0 g/L. The first-order reversible kinetic model and Langmuir isotherm model were resulted in high correlation coefficients and described well the adsorption of Cd(II) onto PGCP-COOH. The complete removal of 22.4 mg/L Cd(II) from fertilizer industry wastewater was achieved by 2.0 g/L PGCP-COOH. The reusability of the PGCP-COOH for several cycles was demonstrated using 0.1 M HCl solution.

Keywords Coir pith · Graft co-polymerization · Cadmium(II) · Adsorption · Desorption

Cadmium and its compounds enter into the water bodies through activities associated with different industries such as electroplating, pigments, batteries, metallurgical products, ceramics, alloys and electronics. Cadmium(II) is considered as a priority pollutant by the US Environmental Protection Agency. Due to its high toxicity, the permissible limit for Cd(II) as described by WHO is 0.01 mg/L. Various methods are available for the removal of Cd from wastewaters including chemical precipitation, membrane filtration, ion exchange, adsorption, cementation, solvent extraction and reverse osmosis. Among these, adsorption remains popular because of easy operation, low energy consumption, simple maintenance and large capacity (Lam et al. 2007). Numerous adsorbents such as activated carbons, agricultural and industrial waste products, clays and hydrous metal oxides have been examined for their potential to remove Cd(II) from wastewaters. (Vazquez et al. 2002; Krishnan and Anirudhan 2003).

Effective use of biomass waste has become one of the promising fields of investigation due to availability of the raw material almost free of cost as well as their environmentally friendly nature. The main disadvantages of these materials are their low resistance to abrasive forces in batch or column operation and leaching of soluble organics during adsorption. To solve these problems and also to improve the adsorption potential different types of chemical treatments such as esterification, phosphorylation, graft copolymerization, and quaternization have been reported. The incorporation of selected functional groups onto the polymer matrix of the chemically modified biomass such as peanut shell (Chamorthy et al. 2001), orange residue (Ghimire et al. 2002), saw dust (Seiban et al. 2006), Chineese weed (Namasivayam and Holl 2005), banana stalk (Shibi and Anirudhan 2006) and banana stem (Noelin et al. 2005) has been reported for the removal of metals from wastewater. The coir process industry produces coir pith, a solid waste biomass that presents a significant disposal problem. Any attempt to reutilize the coir pith will be worthwhile. Coir pith and its modified forms have already found use in metal ion removal from aqueous solutions (Parab et al. 2005; Aniurudhan and Unnithan 2007). This work describes the preparation and application of a new adsorbent, namely poly(hydroxyethylmethacrylate) grafted coir pith with carboxylate functionality for the removal of Cd(II) from water and wastewater.

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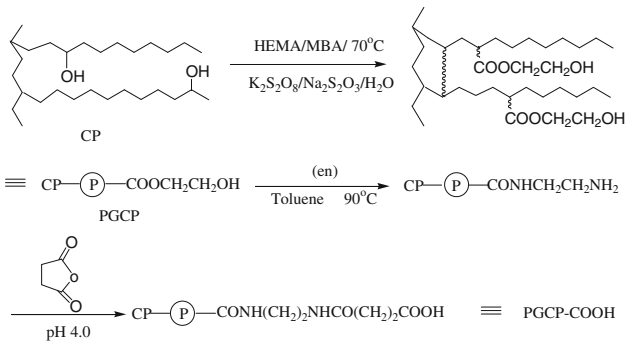
Materials and Methods

Analytical grade chemicals were used throughout the experiment. The monomer hydroxyethylmethacrylate (HEMA) was obtained from Fluka (Switzerland). The N,N′-methylenebisacrylamide (MBA) was purchased from Aldrich (WI, USA), while potassium peroxydisulphate ($K_2S_2O_8$), sodium thiosulphate ($Na_2S_2O_3$), ethlenediamine (en) and 1,4-dioxane were obtained from E-Merk, India. A stock solution (1,000 mg/L) of Cd(II) ions was prepared by dissolving an accurately weighed amount of $CdCl_2{\cdot}2H_2O$ (Fluka) in distilled water. Fourier transform infrared (FTIR) measurements were performed on a Shimadzu FTIR 1801 spectrophotometer. The specific surface area of the adsorbent was determined N_2 adsorption data at 77 K with a Quantasorb surface area analyzer (QS/7). A systronic micro processor pH meter (model 362) was used for pH measurements. A temperature controlled water bath shaker (Labline, India) was used for shaking all the solutions. The concentration of Cd(II) in solutions before and after adsorption was measured using a GBC Avanta (model A 5450) atomic absorption spectrometer (AAS) at 228. 8 nm with 3 mA Lamp and 0.5 nm slit width. The minimum detectable concentration corresponding to 0.01 absorbance or 98.0% transmittance is 0.01 mg/L.

The coir pith was collected from a local coir industry situated in Trivandrum city, India and was washed several times with distilled water to remove the water soluble particles. It was then dried at 80°C and sieved between $-80 + 230$ mesh size using standard sieves. The sensitive component for graft copolymerization might be the methyl hydroxyl groups of the cellulose units present in coir pith (CP). The general procedure adopted for the preparation of adsorbent is presented in Scheme 1. About 10 g of coir pith was immersed in 200 mL distilled water in a 1 L three necked reaction flask, and was treated with about 2 g of MBA, 0.2 g of $Na_2S_2O_3$ and 1 g of $K_2S_2O_8$. The contents were stirred well and to this mixture 25 g of HEMA was added and stirred vigorously at about 70°C in a water bath. The solid mass obtained was extracted with water to remove the homopolymer and dried at 80°C in an air oven. The grafted yield was found to be 88.0%. The dried polymer grafted coir pith (PGCP) was then refluxed with ethlenediamine (en) continuously for about 8 h and the product was washed with toluene and dried. A known amount of the above product was then refluxed with an equal amount of succinic anhydride in 1,4-dioxan (100 mL) for about 6 h at 90°C. The product obtained was then washed with 1,4-dioxan, followed by water and ethanol. The carboxylic acid bound PGCP (PGCP-COOH) was collected, dried, ground and sieved to 0.096 mm size.

Batch adsorption experiments were performed in 100 mL Erlenmeyer flasks with agitation provided by a



Scheme 1 Preparation of PGCP-COOH

temperature controlled water bath flask shaker. Kinetic studies were conducted at room temperature (30°C) in a water bath shaker. 50 mL of aqueous solution with various concentrations of Cd(II) was placed in a flask containing 0.1 g adsorbent. The initial pH of the solution was adjusted by adding HCl or NaOH using a pH meter. The contents were shaken at 200 rpm. The progress of the adsorption was noted at different time intervals till the attainment of saturation. Aliquots of the liquid samples were withdrawn at predetermined intervals and centrifuged. The residual Cd(II) concentrations were analyzed using AAS. The amount of Cd(II) adsorbed was calculated from the deference between the initial and final concentrations of metal ions in equilibrium solutions.

The effect of pH on Cd(II) adsorption was conducted by the same batch adsorption procedures described above except that the solution pH was adjusted to 2.0–8.0 at 30°C. For isotherm experiments the concentration of Cd(II) solution ranged from 25 to 300 mg/L. For comparison, a commercial carboxylate functionalized cation exchanger Ceralite IRC-50 obtained from the Central Drug House, Mumbai, India was used. Isotherm experiments were also conducted using Ceralite IRC-50.

To test the reusability of the adsorbent, adsorption desorption experiments were conducted with 0.1 M HCl in four cycles using the same adsorbent. Cd(II) loaded PGCP-COOH was agitated with 50 mL of 0.1 M HCl for 3 h at 30°C. The final concentration of Cd(II) in aqueous solution was determined using AAS as described above. The percentage of desorption was calculated from the amount of Cd(II) adsorbed on PGCP-COOH and the final Cd(II) concentration in the desorption medium. All the adsorption experiments were performed in triplicate and the results were averaged. The maximum variation with batch adsorption data among triplicate values is 3.0%. The kinetic and isotherm data were analyzed using standard kinetic and isotherm models. The kinetic and isotherm parameters and the model fit were demonstrated by the non-linear regression method using Solver add-in function of the Microsoft Excel.

Results and Discussion

The surface and physical properties of the adsorbent were determined using the standard methods described in earlier publication (Manohar et al. 2006). The characteristics of the PGCP-COOH are: surface area, 47.3 m^2/g; total pore volume,0.44 mL/g; pH $_{PZC}$, 5.5; total acidity, 1.82 meq/g; carboxylate content, 1.44 meq/g; cation exchange capacity, 1.81 meq/g; particle size, 0.096 mm and apparent density, 0.88 g/mL.

The FTIR spectra of coir pith and PGCP-COOH are shown in Fig. 1. The spectrum of coir pith showed a band at 3,282 cm^{-1} indicating the hydrogen bonded O–H stretching vibrations in the cellulose structure of coir pith. The bands at 2,922 and 1,782 cm^{-1} represent the C–H stretching from CH_2 group and C=O stretching of the hemicellulose. The band at 538 cm^{-1} is assigned to β-glycosidic linkage. The shift of stretching frequency corresponding to the presence of –OH groups at 3,282 cm^{-1} in coir pith to 3,745 cm^{-1} in PGCP-COOH indicates the involvement of hydroxyl groups in the grafting of HEMA on coir pith. For PGCP-COOH, the band at 1,574 cm^{-1} can be ascribed to the asymmetrical stretching vibration of C=O of the carboxyl group, while the band at 1,755 cm^{-1} is probably due to the stretching vibration of C=O of the COOH group. The band at 1,560 cm^{-1} is attributed to the N–H bending vibrations 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 effect of adsorbent dose on the extent of Cd(II) adsorption shows that PGCP-COOH exhibits higher adsorption capacity than that of coir pith (Fig. 2). The amounts of coir pith and PGCP-COOH needed to achieve almost 100% removal of Cd(II) in a solution containing 50 mg/L were 3.0 and 1.5 g/L, respectively. The data clearly indicate that PGCP-COOH is 2 times more effective than coir pith for the removal of Cd(II) from aqueous solution. The values of pH $_{PZC}$ for coir pith and PGCP-COOH were found to be 6.8 and 5.5, respectively. The decrease in the pH $_{PZC}$ after chemical modification indicates that the surface become more negative and this helps to adsorb positively charged Cd(II) ions through electrostatic interaction. Since PGCP-COOH had higher adsorption efficiency than coir pith, subsequent adsorption experiments with Cd(II) were conducted only on PGCP-COOH.

The effect of pH on the adsorption of Cd(II) was examined in the pH range 2.0–8.0 using two different initial concentrations of 25 and 50 mg/L as shown in Fig. 3. The removal of Cd(II) ions from aqueous solution was affected by the solution pH. It increases with the increase in pH reaching a maximum adsorption at pH range 6.0–8.0. A maximum removal of 99.9% and 95.4% was observed for an initial concentration of 25 and 50 mg/L, respectively at pH 6.0. At the pH range 2.0–6.0, it is believed that ion exchange and complexation processes are the major mechanisms for the removal of Cd(II) ions.

$$2\text{PGCP-COOH} + Cd^{2+} \rightleftharpoons (\text{PGCP-COOH})_2Cd + 2H^+ \quad (1)$$

The carboxylic sites on the adsorbent can be appreciably deprotonated at a solution pH between 2.0 and 6.0. Above pH 6, PGCP-COOH was slightly negatively charged and Cd(II) ions were positively charged. Along with Cd^{2+}, $Cd(OH)^+$ and $Cd(OH)_2$ species are also present at the pH range between 6.0 and 8.0 (Vazquez et al. 2002). Hence adsorption is due to the electrostatic force of attraction between the PGCP-COO^- surface and Cd^{2+} ions.

The amount of Cd(II) adsorbed on unit mass of PGCP-COOH showed a positive trend with time of contact (Fig. 4). The results indicate a rapid initial uptake rate of Cd(II) at the beginning and, therefore the adsorption rate decreased gradually. Equilibrium time for the adsorption of Cd(II) on PGCP-COOH at various initial concentrations was found to be 3 h. This indicates that equilibrium time is

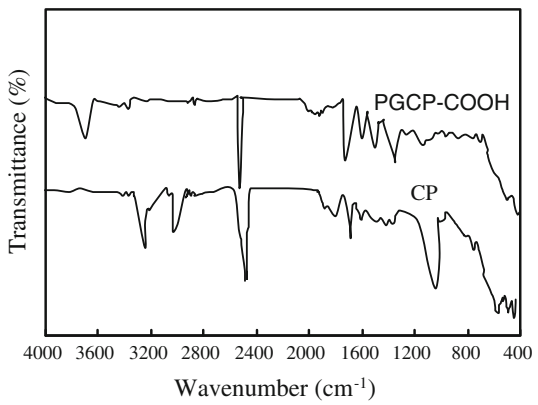


Fig. 1 FTIR spectra of PGCP-COOH and coir pith (CP)

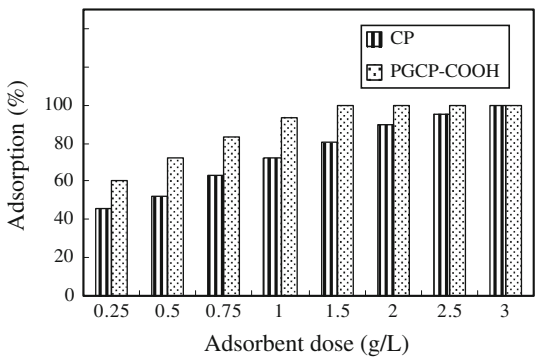


Fig. 2 Effect of adsorbent dose on the adsorption of Cd(II) onto coir pith (CP) and PGCP-COOH

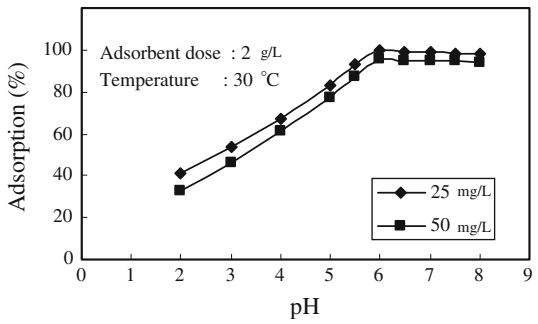


Fig. 3 Effect of pH on the adsorption of Cd(II) onto PGCP-COOH

independent of initial concentration. The curves obtained were single and smooth suggests monolayer adsorption of Cd(II) on PGCP-COOH. The initial faster rate of Cd(II) adsorption may be explained by the large number of adsorption sites available for adsorption. The initial bare surface, the sticking probability is large, and consequently, adsorption proceeded with a high rate. The slower adsorption rate in the second stage is probably due to the diffusion of metal ions into the interior structure of the adsorbent material. For all subsequent adsorption experiments the contact time was maintained for 3 h to ensure that equilibrium could be achieved.

Kinetics of adsorption was modeled by the first-order-reversible rate equation (Lai et al. 2002):

$$\text{In}\ [C_t/C_o] = -k_{ad}[S_s/V]t \qquad (2)$$

where C_t is the Cd(II) concentration (mg/L) at time t, C_o is the initial Cd(II) concentration in mg/L, V is the volume of the solution placed in contact with the adsorbent, k_{ad} is the rate constant and S_s is the outer surface of adsorbent per unit volume of the particle free slurry (cm^{-1}) and is

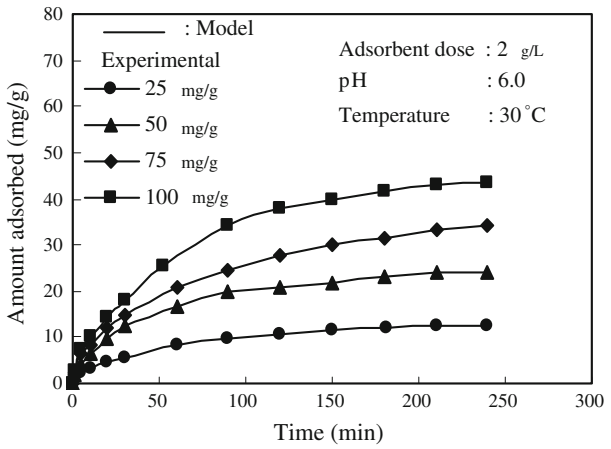


Fig. 4 Effect of contact time on the adsorption of Cd(II) onto PGCP-COOH at different concentrations and comparison of first-order kinetic model with the observed data

calculated as, $S_s = 6m/[dp\ \rho_p\ (1-\varepsilon_p)]$, where dp is the particle diameter (cm), ρ_p is the density of the adsorbent (g/L), ε_p is the porosity of the 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 corresponding to Eq. 2 were found to be 10.08×10^{-3}, 7.30×10^{-3}, 5.20×10^{-3} and 4.61×10^{-3} cm/s at an initial concentration of 25, 50, 75, and 100 mg/L, respectively. The high regression constants (>0.995) and low normalized standard deviation (<5%) indicate that the kinetic data were well correlated to the first-order rate equation described by Lopez et al. (2003).

The effect of ionic strength on Cd(II) adsorption in PGCP-COOH was studied at different concentrations of NaCl. The adsorption percentage of Cd(II) with NaCl concentration of 0.001, 0.005, 0.05, 0.01 and 0.1 M was found to be 91.1%, 87.2%, 79.5%, 68.1% and 61.0%, respectively at an initial concentration of 50 mg/L. The decreasing trend in adsorption with increasing ionic strength indicates the role of electrostatic interactions in adsorption process. Higher ionic strength creates a higher shielding effect for metal ions at the surface of the PGCP-COOH causing a reduction in adsorption. The competition between Na^+ ions and metal ions for the active sites on PGCP-COOH is responsible for decrease in the sorption at higher ionic strength. The modification of the Cd(II) species is another important factor leading to a decrease in adsorption with increase in ionic strength. It has been reported by earlier workers (Benjamin and Leckie 1982) that an increase in chloride concentration reduces the Cd^{2+} and $Cd(OH)^+$ species due to the formation of chloro-complexes. Cadmium forms some stable chloro-complexes, namely $CdCl^+$, $CdCl_2$ and $CdCl_3^-$, which do not appear to be adsorbed to the same extent as Cd^{2+} and $Cd(OH)^+$ ions.

The analysis of equilibrium isotherm data is important in developing an equation that describe the results and can be used in designing an adsorption system. In the present investigation the data were found to fit with the well-known Langmuir isotherm. Langmuir adsorption isotherm is based on the assumption of monolayer coverage of the adsorbate on the surface of the adsorbent and no subsequent interaction among adsorbed molecules. In Fig. 5 adsorption isotherm was approximated by the Langmuir isotherm model, which was represented by the following equation.

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \qquad (3)$$

where Q_0 and b are Langmuir constants related to monolayer sorption capacity and the energy of adsorption respectively, q_e is the observed adsorption capacity (mg/g). The values of Q^0 and b were determined by a non-linear

regression analysis using ORIGIN program (Version 7.5) and were found to be 49.86 mg/g and 0.28 L/mg, respectively at 30°C. The high correlation coefficient, R^2 (0.99) and low χ^2 (0.86) value indicate that the adsorption process is best fitted to the Langmuir equation. The Langmuir plot for Cd(II) adsorption onto PGCP-COOH based on Eq. 3 is shown in Fig. 5. The Langmuir model fits the experimental adsorption data very well indicates that the adsorbed layer is one molecule thick and that the adsorbed layer has the same energies and enthalpies of adsorption.

For comparison, adsorption isotherm experiments were also performed using a commercial carboxylic acid functionalized cation exchanger Ceralite IRC-50. The data so obtained is converted to Langmuir isotherm as shown in Fig. 5. The higher value of R^2 (0.99) and lower value of χ^2 (1.07) obtained for Langmuir model indicates that this model could define the experimental results in the Ceralite IRC-50–Cd(II) system. The calculated values of Q^0 and b were 47.46 and 0.11 L/mg, respectively, which were comparable with those calculated for PGCP-COOH.

A real industry wastewater sample collected from a fertilizer industry situated in Cochin city, India, was treated with PGCP-COOH. The waste water sample was characterized using standard methods (AmericanPublicHealth Association (APHA) 1992). The water sample contains apart from Cd(II) (22.4 mg/L), other metal ions based on cations such as Pb^{2+} (0.3 mg/L), Hg^{2+} (0.2 mg/L) Mg^{2+} (20.3 mg/L),Ca^{2+} (10.2 mg/L) Na^{+} (35.1 mg/L) and K^{+} (69.4 mg/L), and anions such as Cl^{-} (115.5 mg/L), SO_4^{2-} (77.3 mg/L), NO_3^{-} (73.4 mg/L), F^{-} (3.3 mg/L), CO_3^{2-} (8.7 mg/L), PO_4^{3-} (16.6 mg/L) and chemical oxygen demand COD (207.9 mg/L). The effect of adsorbent dose on Cd(II) removal from wastewater was investigated. Adsorbent dose was varied from 0.5 to 5 g/L. Initially the increase in adsorbent dose from 0.5 to 1.5 g/L, Cd(II) removal increased significantly (Figure not shown). No appreciable increase in adsorption was observed beyond adsorbent dose of 1.5 g/L. Complete removal of Cd(II) from 1.0 L wastewater sample containing 22.4 mg/L of Cd(II) was achieved with 2 g/L of PGCP-COOH. The possible release of any organics into solution during Cd(II) adsorption by PGCP-COOH was also investigated. For this the amount of COD in water sample before and after adsorption was determined by means of dichromate method (AmericanPublicHealth Association (APHA) 1992). Even when the quantity of PGCP-COOH ranged between 0.5 and 2.0 g/L, the amount of COD varied between 26.5 and 56.6 mg/L. These values are lower than that of the initial amount present in the water sample (207.9 mg/L). Graft copolymerization induces a stabilization of the hydrolysable compounds of coir pith by creating new bonds on constitutive units and make the coir pith able to adsorb Cd(II) ions without releasing any organic substances.

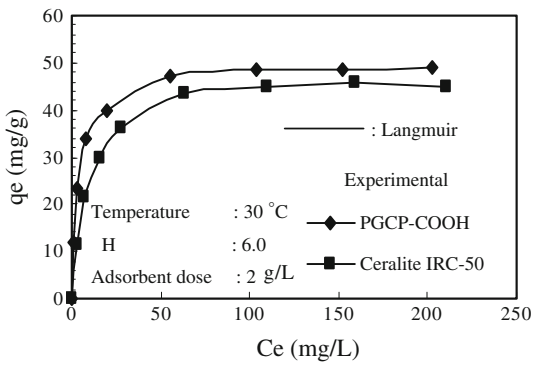


Fig. 5 Comparison of the model fit of the Langmuir isotherm data for the adsorption of Cd(II) onto PGCP-COOH and Ceralite IRC-50 at 30°C

Since ion exchange is generally reversible, the Cd(II) desorption was executed using HCl solution. The desorption efficiency of 0.005, 0.01, 0.05, 0.1 and 0.2 M HCl solutions was found to be 65.3, 72.6, 85.1, 94.5 and 96.3%, respectively. Therefore the optimum concentration of HCl was selected to be 0.1 M in terms of economic process. To assess the reusability of the spent adsorbent, four adsorption–desorption cycles with the same adsorbent using 0.1 M HCl as the desorbing agent were performed. After the four cycles the adsorption capacity of PGCP-COOH decreased from 99.9% to 96.3% while the recovery of Cd(II) decreased from 96.3% to 83.2%. At the end of fourth cycle the recovery of Cd(II) was slightly decreased, while the adsorption capacity was relatively maintained. These results indicate that some of the adsorbed Cd(II) species penetrate into the inner cavities and forms inner-sphere complexes with the oxygen atom of the adsorbent.

In the present study, a novel adsorbent, poly (hydroxyethylmethacrylate)-grafted coconut coir pith having carboxylate functional groups (PGCP-COOH) was prepared and its efficiency in removing Cd(II) was tested. The maximum removal of Cd(II) occurs at pH range 6.0–8.0. The equilibrium time was reached within 3 h. The adsorption follows first-order kinetics. The equilibrium isotherm data were fitted well by the Langmuir isotherm as evidenced from the good agreement between the experimental and calculated values. The quantitative removal of Cd(II) from a fertilizer industry wastewater sample confirmed the stability of the adsorbent for water purification. The adsorbed Cd(II) was quantitatively desorbed using 0.1 M HCl and the adsorbent can be reused up to four cycles without loss of adsorption capacity.

The results of the present investigation illustrate that PGCP-COOH can be used as an adsorbent for the effective removal of Cd(II) from aqueous solutions and industrial effluents. Detailed studies will be needed 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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