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[Research]

Application of synthetic polymers as adsorbents for the removal of cadmium from aqueous solutions: Batch experimental studies

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ABSTRACT

In the present study seven synthetic polymers were used as adsorbents for the removal of Cd(II) from aqueous solution. The equilibrium studies were systematically carried out in a batch process, covering various process parameters that include agitation time, adsorbent dosage, and pH of the aqueous solution. The analyzing system was an atomic absorption spectrometer (Perkin-Analyst 100). It was observed in adsorption and desorption tests that synthetic polymers showed significant pH dependence, which affected the removal efficiency, robustly. Adsorption behavior was found to follow Freundlich and Longmuir isotherms. A regeneration study was also carried out.

Keywords: *Cadmium, Adsorption, Synthetic polymers, Heavy metals, Wastewater treatment.*

INTRODUCTION

The pollution of water and soil with metal cations has increased dramatically in the last 50 years as a consequence of the expedition of industrial activities. The well-established toxicity of metals in solution at sufficiently high concentrations affects humans, animals and vegetation (Abbasi *et al*. 1998). Due to the problems mentioned, attention has been focused on the various adsorbents, which have metal binding capacities and are able to remove unwanted heavy metals from contaminated water at low-costs (Pipšika *et al*. 2010; Kumar Bajpai *et al*. 2009 and Saberyan *et al*. 2010). Because of their low cost and local availability, natural materials such as chitosan, zeolites, clays, or certain waste products from industrial operations such as fly ash, coal and oxides are classified as low-cost adsorbents (Turner *et al*. 1998; Naseem & Tahir 2001; Pusch 1992 and Khan *et al*. 1995). A suitable adsorbent for adsorption processes of pollutants should meet several requirements :(i) efficient for removal of a wide variety of target pollutants; (ii) high capacity and rate of adsorption; (iii) important selectivity for different concentrations; (iv) granular type with good surface area; (v) high physical strength; (vi) able to be regenerated if required; (vii) tolerant for a wide range of wastewater parameters; and (viii) low-cost. The natural sorbents (polysaccharides) are low-cost materials obtained from natural raw resources. These materials are versatile and allow the sorbents to be used under different forms and can be regenerated easily. But there are some limitations in adsorption by natural adsorbent (Chandra & Rustgi 1998; Crini 2003; Cao *et al*. 2001; Kurita 2001; Guibal *et al*. 2006; Ajmal *et al*. 1998 and Lee & Davis 2001). The adsorption properties of the adsorbents depend on the different sources of raw materials in spite of the extreme variability of industrial waste water must be taken into account in the design of any polysaccharide system. Each type of pollutant may need its own particular polysaccharide. The choice of adsorbent depends on the nature of pollutant. On the other hand, the efficiency of adsorption depends on physicochemical characteristics such as porosity, surface specific area and particle size of sorbent. Another problem with polysaccharide based materials is their poor physicochemical characteristics in particular porosity (Mcafee *et al*. 2001; Delval *et al*. 2005 and Mi *et al*. 2002).

The use of synthetic adsorbant polymers in wastewater treatment has been investigated by several authors (Boenig *et al*. 1980 and Ferraro 1987.) These adsorbers composed of synthetic polymer and ligand, wherein the metal ions are bound to the polymer ligand by a coordinate bond. A ligand contains anchoring sites like nitrogen, oxygen or sulfur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability (Kantipuly *et al*. 1990; Arsalani *et al*. 2009 and Kaliyappan & Kannan 2000). During the last few years, attempts were made to improve these adsorber polymers which originally were developed on the basis of ion exchange resins (Dedek *et al*. 1992). On the other hand, the use of new technologies allowed the production of highly porous polymers with a specific surface of 800–1500 m^2g^{-1} which is similar to the surface of activated carbon (Schröder & Radeke 1995).

The main objective of this work is to develop and apply seven synthetic polymers as potential sorbents for removal and determination of Cd(II) in polluted solutions. The purpose also includes the investigation of the effects of pH, equilibrium time, and other parameters on the removal efficiency. Adsorption isotherms were also investigated.

MATERIALS and METHODS

Start materials were obtained as follows: poly(vinyl pyridine) (PVP), N,N'-methylenebis (acrylamide) (MBAAm-N,N'), poly(acrylamide) (PAAm), benzyl chloride and gum arabic all from Merck or Fluka. The following inorganic materials were used: $Cd(NO_3)_2$ (Merck), HCl 37% and NaOH 99.5% (Fluka). All solutions for experiments were prepared with distillated water. The used adsorbents obtained by blending of the polymers with given ratios are as follows: P1 (PVP + 10% MBAAm-N,N'), P2 (PVP + PAAm (1:1) + 10% MBAAm-N,N'), P3 (PAAm + 10% MBAAm-N,N'), P4 (PAAm + gum arabic (1:5)), P5 (30% PVP + 30% benzyl chloride + 30% MBAAm-N,N'), P6 (30% PVP + 30% benzyl chloride + 20% MBAAm-N,N'), P7 (30% PVP + 30% benzyl chloride + 10% MBAAm-N,N').

Adsorption experiments

Adsorption experiments were conducted at a constant temperature (298 k) on a three dimensional shaker during certain time. The solid-liquid system consisted of 50 ml aqueous solution containing Cd(II) (50 ppm) and different dose of adsorbents. After sufficient contact time, the solution was filtered and filtrate was analyzed by atomic absorption spectrometer. Standard solutions containing 1, 20, 50, 100, and 500 ppm Cd(II) were used for calibration.

Apparatus

A Perkin atomic absorption spectrometer (Perkin-Analyst 100) equipped with a deuterium-arc lamp background corrector was used for absorbance measurements at appropriate wavelengths. The operating conditions were those recommended by the manufacturer, unless specified otherwise. The sample and the acetylene flow rates and the burner height were adjusted in order to obtain the maximum absorbance signal.

RESULTS and DISCUSSION

Effect of pH

pH is an important parameter for adsorption of Cd(II) from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbot during reaction. To examine the effect of pH on the CdII) removal efficiency, the pH of initial solution was adjusted to the corresponding pH value (1.0 – 10.0) using 0.1 M HCl or 0.1 M NaOH. As shown in Fig. 1, the uptake of Cd(II) depends on pH, where optimum metal removal efficiency occurs at pH 10 for all studied polymers. As can be seen from Fig. 1, almost no adsorption of cadmium ions took place on synthetic polymers at pH < 2, probably due to the significant competitive adsorption of hydrogen ions. The adsorption studies at pH >10 were not conducted because of the precipitation of $Cd(OH)_2$ from the solution.

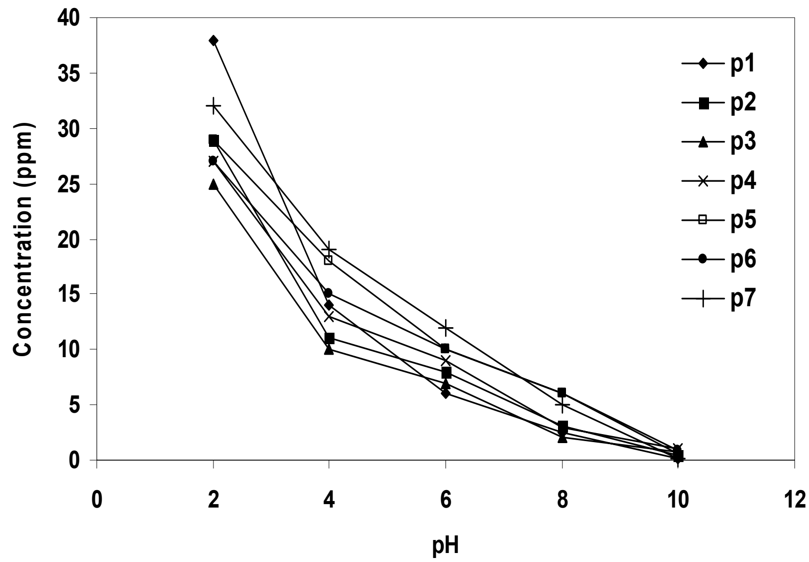

Fig 1. Effect of pH on the Cd(II) removal efficiency using P1-P7 synthetic polymers.

Effect of adsorbent dose

The dependence of Cd(II) sorption on adsorbent dosage was studied by varying the amount of polymers from 0.1 to 0.7 g, while keeping other parameters (pH and contact time) constant. Fig. 2 presents the Cd(II) removal efficiency for seven types of adsorbents used. Form Fig. 2, it can be observed that removal efficiency of the polymers improved with increasing ***adsorbent dosage*** from 0.1 g to 0.4 g. This was expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites. This also suggests that after a certain dose of adsorbent (0.2 g for P1, 0.3 g for P2, P3, P5, P6, P7 and 0.4 g for P4), the maximum adsorption sets in and hence the amount of Cd(II) bound to the adsorbent and the amount of Cd(II) in solution remains constant even with further addition of the dose of adsorbent.

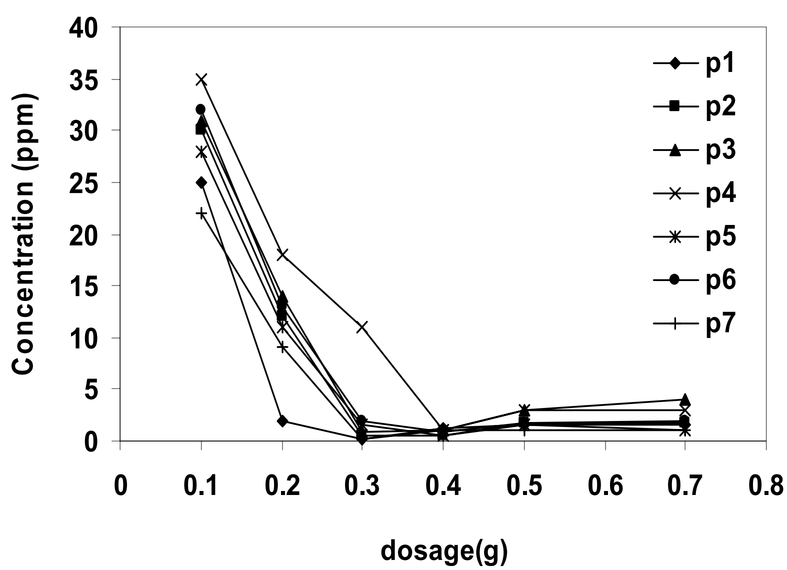

Fig 2. The effect of sorbent dosage on Cd(II) removal efficiency using P1-P7 synthetic polymers.

Effect of agitation time

Results (Fig. 3) indicate that removal efficiency increased with an increase in agitation time. Other parameters such as dose of adsorbent, pH of solution was kept optimum, while temperature was kept at 25 °C. Optimum agitation time for P1, P7 and P2-P6 was found to be 30, 45 and 60 min, respectively. Greater availability of functional groups on the surface of polymers, which is required for interaction polymer and Cd(II), significantly improved the binding capacity and the process proceeded rapidly. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

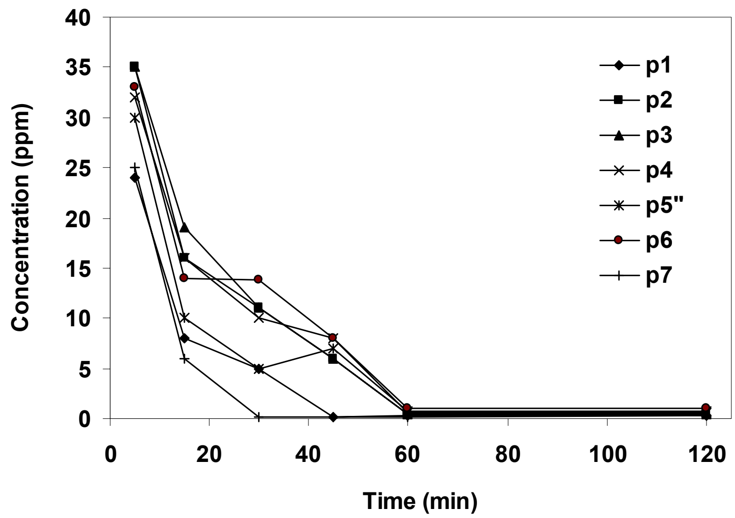

Fig 3. Effect of agitation time on Cd(II) removal efficiency using P1-P7 synthetic polymers.

Adsorption isotherms

The empirical Freundlich relationship does not indicate a finite uptake capacity of the adsorbent. This relationship can be reasonably applied to the low or intermediate concentration ranges. Freundlich isotherm equation is given by:

$$q_e = k_f C_e^{1/n} \quad (1)$$

and is linearized as:

$$\log q_e = \log k_f + 1/n \log C_e \quad (2)$$

Where q_e is the equilibrium adsorption capacity of Cd(II) on the adsorbent (mg/g), C_e the equilibrium Cd(II) concentration in solution (mg/L), k_f Freundlich constant (L/mg), and n is heterogenity factor. The present data in Table 1 shows relatively good linearity for Freundlich relationship. Linearity of the relationship indicates strong binding of Cd(II) to the adsorbents. The values of k_f and n were determined from the slope and intercept of the linear plot of log q_e versus log C_e.

Table 1. Freundlich linear isotherms for the adsorption of Cd(II) using P1-P7 synthetic polymers.

Adsorbent type	Equation	Regression coefficient
P1	log qe = 0.5789 log Ce - 0.7789	R2 = 0.9963
P2	log qe = 0.5125 log Ce - 0.7568	R2 = 0.9879
P3	log qe = 0.6125 log Ce - 0.8954	R2 = 0.9911
P4	log qe = 0.6042 log Ce - 0.7986	R2 = 0.9821
P5	log qe = 0.5897 log Ce - 0.7998	R2 = 0.9941
P6	log qe = 0.5612 log Ce - 0.8142	R2 = 0.9861
P7	log qe = 0.5588 log Ce - 0.7889	R2 = 0.9819

Langmuir isotherm is the most widely used two-parameter equation. The relationship is of the form:

$q_e/q_m = bC_e/ (1+bC_e)$ (3)

or

$C_e/q_e=C_e/q_m+1/bq_m$ (4)

q_m the maximum capacity of adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg). Langmuir isotherm for the present data is presented in Table 2. q_m and b are calculated from the slope ($1/q_m$) and intercept ($1/bq_m$) (Table 3). The isotherm lines have good linearity.

Table 2. Langmuir linear isotherms for the adsorption of Cd(II) using P1-P7 synthetic polymers.

Adsorbent type	Equation	Regression coefficient
P1	$C_e/q_e = 0.0316\ C_e + 4.7846$	$R^2 = 0.9929$
P2	$C_e/q_e = 0.0409\ C_e + 4.7623$	$R^2 = 0.9984$
P3	$C_e/q_e = 0.0412\ C_e + 4.7459$	$R^2 = 0.9899$
P4	$C_e/q_e = 0.0369\ C_e + 4.8152$	$R^2 = 0.9905$
P5	$C_e/q_e = 0.0394\ C_e + 4.8596$	$R^2 = 0.9990$
P6	$C_e/q_e = 0.0514\ C_e + 4.7955$	$R^2 = 0.9878$
P7	$C_e/q_e = 0.0387\ C_e + 4.6946$	$R^2 = 0.9869$

Table 3. Langmuir and Freundlich constants for the uptake of cadmium using P1-P7 synthetic polymers.

Adsorbent type	Freundlich constants		Langmuir constants	
	n	k_f	q_m	b
P1	1.73	0.17	31.6	0.007
P2	1.95	0.17	24.4	0.008
P3	1.63	0.13	24.3	0.009
P4	1.66	0.16	27.1	0.008
P5	1.70	0.16	25.4	0.008
P6	1.78	0.15	19.4	0.011
P7	1.79	0.16	25.8	0.008

Desorption studies

For potential practical applications, the regeneration and reuse of an adsorbent are important. From the pH study, it has been found that the adsorption of cadmium ions on all polymers tested at pH ≤ 2.0 was negligible. This suggested that desorption of cadmium ions from these polymers was possible around pH 2.0. Therefore, HCl solutions of different pH (2.5, 2.0 and 1.5) were used to examine the desorption study. It was found that the desorption percentages were 79, 91, and 93% for P1 adsorbent in the HCl solutions of pH 2.5, 2.0, and 1.5, respectively. The higher desorption efficiency at lower pH value could be referred to the sufficiently high hydrogen ion concentration, which led to the strong competitive adsorption.

CONCLUSION

Seven synthetic polymers were used for removal of cadmium ions from aqueous solutions. Based on the results, the P1 polymer was found as the best sorbent for adsorption of Cd(II) due to higher q_m and lower amount of adsorbent (0.2 g). All polymeric sorbents showed significant pH dependence, which had a considerable effect on the cadmium removal. According to the collected results, the P1 polymer exhibited high performance as an adsorbent for removal of Cd(II) from aqueous solutions. It has been composed of poly(vinyl pyridine) and N,N'-methylenebis (acrylamide). Our findings showed that this sorbent has more affinity for cadmium than others. Adsorption of Cd(II) by P1-P7 are dependent on contact time, pH solution and dosage of adsorbent. The adsorption data fit in both Freundlich and Langmuir isotherms. In addition, acid solutions at pH≤2 was suitable for desorption of cadmium ions and the reusability of synthetic polymers were good.

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کاربرد پلیمرهای سنتزی به عنوان جاذب برای حذف کادمیم از محلول‌های آبی: مطالعات آزمایشگاهی ناپیوسته

ر. شمشادی، م. آروند، ا.ا. افندیف و ن.ا. زینالف

چکیده

در این مطالعه هفت پلیمر سنتزی به عنوان جاذب برای حذف Cd(II) از محلول آبی استفاده شدند. بررسی‌های تعادلی به شیوه سیستماتیک و در یک فرآیند ناپیوسته انجام گردید بطوریکه عوامل مختلفی از جمله زمان همزدن، میزان جاذب و محلول آبی را در بر می‌گرفت. سیستم آنالیزکننده یک دستگاه اسپکترومتر جذب اتمی (Perkin-Analyst 100) بود. در بررسی‌های جذب و واجذب مشاهده شد که پلیمرهای سنتزی وابستگی شدیدی به pH داشتند که بر روی کارایی حذف شدیداً موثر بود. رفتار جذبی از همدماهای فروندلیش و لانگمویر پیروی می‌نمود. مطالعاتی در زمینه بازیابی جاذب نیز انجام شد.