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Synthetic Polymers as Adsorbents for the Removal of Cd(II) from Aqueous Solutions

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In the present investigation seven synthetic polymers are used as adsorbents for the removal of Cd(II) from aqueous solution. The equilibrium studies are systematically carried out in a batch process, covering various process parameters that include agitation time, adsorbent dosage and pH of the aqueous solution. It was observed in adsorption and desorption tests that the synthetic polymers showed significant pH dependence, which affect the removal efficiency, robustly. Adsorption behaviour is found to follow Freundlich and Langmuir isotherms. A regeneration study was also carried out.

Key Words: 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 consequence of the expiation of industrial activities. The well-established toxicity of metals in solution at sufficiently high concentrations affects humans, animals and vegetation[1]. Due to the problems mentioned, attention has been focused on the various adsorbents, which have metal binding capacities and are able to remove undesired heavy metals from contaminated water at low-cost[2-4]. 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[5-8]. A suitable adsorbent for adsorption processes of pollutants should meet several requirements: (i) efficient for removal of a wide variety of target pollutant; (ii) high capacity and rate of adsorption; (iii) important selectivity for different concentrations; (iv) granular tape with good surface area; (v) high physical strength; (vi) able to 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 adsorbents[9-15]. The adsorption properties of the adsorbents depend on the different sources of raw materials in spite of the extreme variability of industrial waste water taken in to 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 hands, the efficiency of adsorption depends on physicochemical characteristic such as porosity, surface specific area and particle size of sorbent. Another problem with polysaccharide based materials is their poor physico-chemical characteristics in particular porosity[16-18].

The use of synthetic adsorber polymers in wastewater treatment has been investigated by several authors[19,20]. 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[21-23]. During the last few years, attempts were made to improve these adsorber polymers which originally were developed on the basis of ion exchange resins[24]. On the other hand, the use of new technologies allowed the production of highly porous polymers with a specific surface of 800-1500 m^2 g^{-1} which is similar to the surface of activated carbon[25].

The main objective of this work is to develop and application of 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.

EXPERIMENTAL

All the 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 % (Fluka), NaOH 99.5 % (Fluka). All solutions for experiments were prepared with distillated water. The used polymers obtained 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 in 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.

A Perkin atomic absorption spectrometer (Perkin-Analyst 100) equipped with a deuterium-arc lamp background corrector was used for absorbance measurements at appropriate wave-lengths. 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 adsorbat during reaction. To examine the effect of pH on the Cd(II) 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 precipi-tation of $Cd(OH)_2$ from the solution.

Effect of adsorbent dose: The dependence of Cd(II) sorption on adsorbent dosage was studied by varying the amount of polymers from 0.1-0.7 g, while keeping other parameters (pH and contact time) constant. Fig. 2 presents the Cd(II) removal efficiency for all the seven types of adsorbents used. Form Fig. 2, it can be observed that removal efficiency of the polymers improved with increasing dose from 0.1-0.4 g. This is 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.

Effect of agitation time: 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 298 K. Optimum agitation time for P1, P7 and P2-P6 was found to be 30, 45

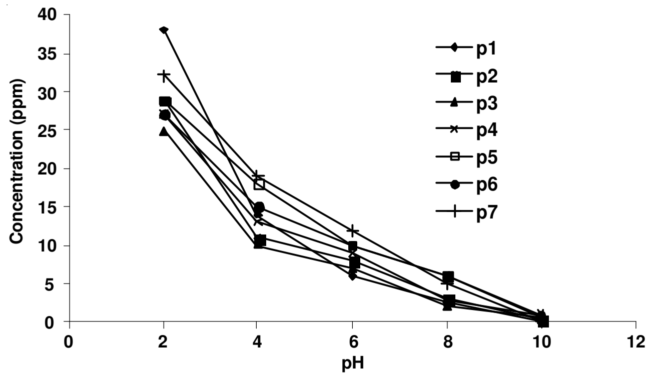

Fig. 1. Effect of pH on the Cd(II) removal efficiency using P1-P7 synthetic polymers

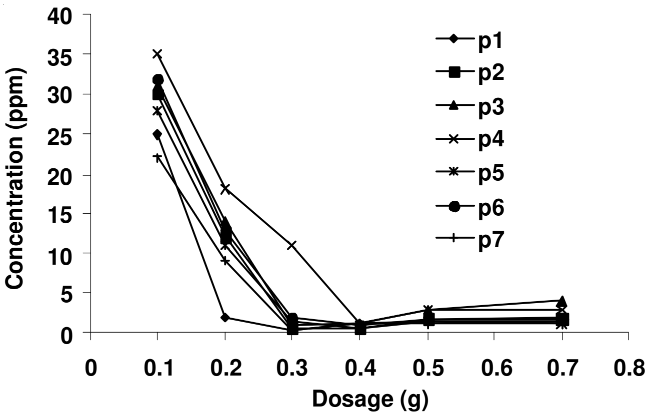

Fig. 2. Effect of sorbent dosage on Cd(II) removal efficiency using P1-P7 synthetic polymers

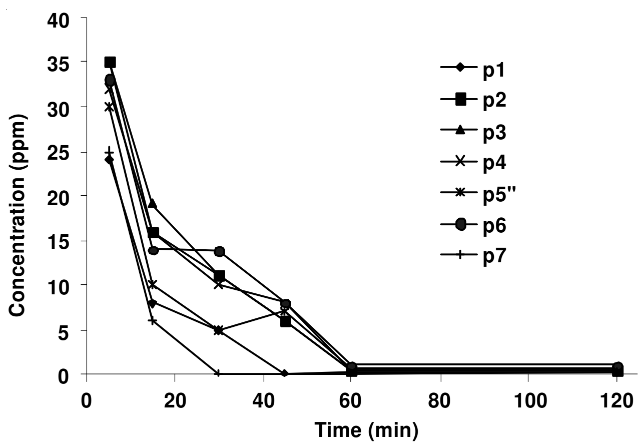

Fig. 3. Effect of agitation time on Cd(II) removal efficiency using P1-P7 synthetic polymers

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.

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 heterogeneity 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	$\log q_e = 0.5789 \log C_e - 0.7789$	$R^2 = 0.9963$
P2	$\log q_e = 0.5125 \log C_e - 0.7568$	$R^2 = 0.9879$
P3	$\log q_e = 0.6125 \log C_e - 0.8954$	$R^2 = 0.9911$
P4	$\log q_e = 0.6042 \log C_e - 0.7986$	$R^2 = 0.9821$
P5	$\log q_e = 0.5897 \log C_e - 0.7998$	$R^2 = 0.9941$
P6	$\log q_e = 0.5612 \log C_e - 0.8142$	$R^2 = 0.9861$
P7	$\log q_e = 0.5588 \log C_e - 0.7889$	$R^2 = 0.9819$

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

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

or

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

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.

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 suffi ciently high hydrogen ion concentration, which led to the strong competitive adsorption.

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

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) in shorter contact time (0.5 h) 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. Adsorption of Cd(II) by P1-P7 are depended 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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