STUDY OF Cd(II) ADSORPTION FROM AQUEOUS SOLUTIONS ON THE SYNTHETIC POLYMERS

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In the present study 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 synthetic polymers showed significant pH dependence, which affected the removal efficiency robustly. Adsorption behavior is found to follow Freundlich and Longmuir isotherms.

INTRODUCTION

The pollution of water and soil with metal cations has increased dramatically in the last 50 years as a consequence of the expiation of industrial activities. The well-established toxicity of metals in the solution at sufficiently high concentrations affects humans, animals and vegetation [1]. Due to the problems mentioned, attention has been focused on various adsorbents, which have metal binding capacities and are able to remove unwanted heavy metals from contaminated water at low - cost [2,3]. A suitable adsorbent for adsorption processes of pollutants should meet several requirements: efficient for removal of a wide variety of target pollutant; high capacity and rate of adsorption; important selectivity for different concentrations; granular tape with good surface area; high physical strength; able to be regenerated if required; tolerant for a wide rang of wastewater parameters; and 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 the adsorption by natural adsorbent [4-6]. The adsorption properties of the adsorbents depend on different sources of raw materials in spite of the fact that extreme variability of industrial waste water has be taken in to account when designing 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 physicochemical characteristic in particular porosity [7,8].

The use of synthetic adsorber polymers in wastewater treatment has been investigated by several authors [9,10]. These adsorbers are 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 with the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound having coordinating ability [11-13]. During the last few years, attempts were made to improve these adsorber polymers which originally were developed on the basis of ion exchange resins [14]. 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 [15].

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 pH effects, equilibrium time, and other parameters on the removal efficiency. Adsorption isotherms were also analysed.

EXPERIMENTAL

Starting materials were obtained as follows: polyvinylpyridine (PVP), polyvinylpyrrolidone (PVPr) N,N-methylenbisakrylamide (MBAKMD), polyacrylamide (PAKMD), benzyl chloride, gum Arabic all from Merck or Fluka. The following inorganic materials were used: $Cd(NO_3)_2$ (Merck), HCl 37% (Fluka), NaOH 99.5% (Merck). All solutions for experiments were prepared with distillated water. The used polymers were obtained as follows: P1 - (PVPr + 10% MBAKMD), P2 - (PVPr +PAKMD (1:1) + 10% MBAKMD),P3 - (PAKMD + 10% MBAKMD), P4 - (PAKMD + gum arabic (1:5) +10% MBAKMD. The obtaining of PVPr and its copolymers with cameds are described by methodology [16]. P5 - (30% PVP + 30% benzyl chloride + 30% MBAKMD), P6 - (30% PVP + 30% benzyl chloride + 20% MBAKMD), P7 - (30% PVP + 30% benzyl chloride + 10% MBAKMD). And obtaining of PVP, its quaternization with benzylchloride and cross-linking with crossing agent, particularly with MBAKD are synthesized by methodology [17].

Adsorption experiments were conducted at a constant temperature (298 K) on three dimensional shakers within a 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 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 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 DISCUSSIONS

pH is an important parameter for adsorption of Cd(II) from aqueous solution because it affects the solubility of metal ions, concentration of 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 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. From Fig. 1, almost no adsorption of cadmium ions took place on synthetic polymers when 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.

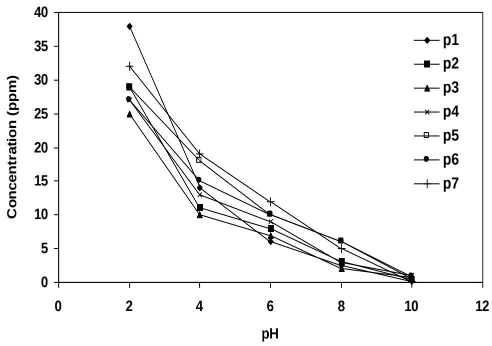

Fig. 1 Effect of pH on the Cd(II) removal efficiency using P1-P7 synthetic polymers.

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.

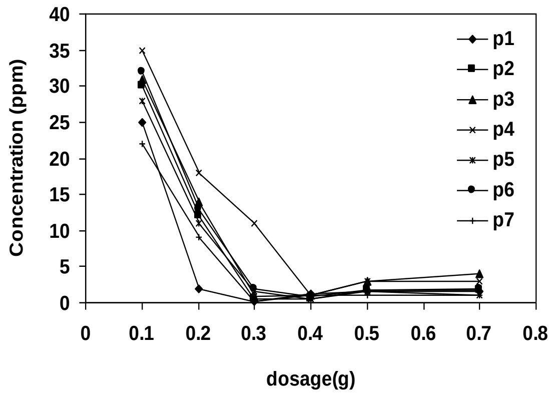

Fig. 2. The effect of sorbent dosage on Cd(II) removal efficiency using P1-P7 synthetic polymers.

Fig. 2, it can be observed that removal efficiency of the polymers improved with increasing dose from 0.1 g to 0.4g. 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 (0.2g for P1, 0.3g for P2, P3, P5, P6, P7 and 0.4g 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 the solution remains constant even with further addition of the dose of adsorbent.

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 ºC. 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.

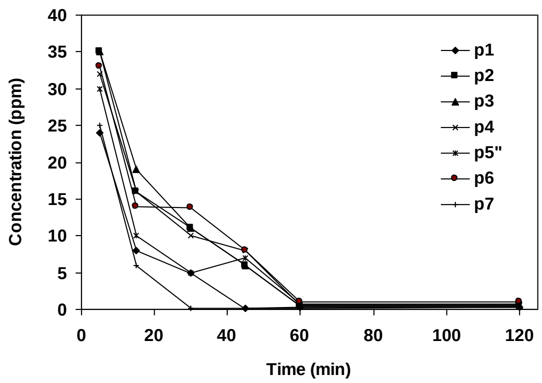

Fig. 3. Effect of agitation time on Cd(II) removal efficiency using P1-P7 synthetic polymers.

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 the 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:

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

or

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

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

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% 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 a potential sorbent for adsorption of Cd(II) in shorter contact time (30 min) 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 higher 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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Cd(II)-nin SULU MƏHLULLARDAN ADSORBSİYASININ SİNTETİK POLİMERLƏRDƏ TƏDQİQİ

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Göstərilən tədqiqat işində sintetik polimerlər adsorbent kimi Cd(II)-nin sulu məhlullarından ayrılmasında istifadə edilmişdir. Müxtəlif parametrlərin, yəni qarışdırılma müddətinin, adsorbentin miqdarının və sulu məhlulların pH-nın adsorbsiya prosesinə təsiri tədqiq edilmişdir. Sintetik polimerlər vasitəsilə adsorbsiya və desorbsiyaya pH əsaslı təsir göstərir, bu da sorbsiya effektivliyini artırır. Müəyyən olunmuşdur ki, adsorbsiya Freyndlix və Lenqmyur izotermləri üzrə baş verir.

ИССЛЕДОВАНИЕ АДСОРБЦИИ Cd (II) ИЗ ВОДНЫХ РАСТВОРОВ НА СИНТЕТИЧЕСКИХ ПОЛИМЕРАХ

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В данном исследовании синтетические полимеры используются как адсорбенты для удаления Cd (II) из водных растворов. Проведены систематические исследования равновесия в серийном производстве, включающие различные параметры процесса, такие как время перемешивания, количество адсорбента и pH водного раствора. В адсорбционных и десорбционных образцах синтетические полимеры оказывают влияние на существенную зависимость pH, которая сильно влияет на эффективность удаления. Обнаружено, что адсорбция происходит согласно изотермам Фрейндлиха и Ленгмюра.