

## Batch experimental studies of Hg(II) ion removal from aqueous solution using seven synthetic polymers

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### ABSTRACT

In this work application of seven synthetic polymers as adsorbents for the removal of Hg(II) from aqueous solution was studied. 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. Variations of Hg(II) concentration in solution have been studied through measuring the amount of DTZ-Hg(II) complex by a double-beam spectrophotometer. Because of absorbance interference of DTZ-Hg(II) complex with DTZ ligands at 480 nm, which is  $\lambda_{\max}$  of the complex, the absorbance peak was checked at 595 nm, which belongs to DTZ ligands. Decreasing of Hg(II) concentration after contacting with the adsorbents expressed the efficiency of these adsorbents in extraction of mercury(II) even in solution with high mercury(II) concentrations. 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 Langmuir isotherms. A regeneration study was also carried out.

**Keywords:** Mercury, Synthetic polymers, Adsorption, Pollution, Wastewater treatment

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### 1. INTRODUCTION

The pollution of water occurs due to the existence of toxic metals and organic compound and it leads to serious problems for humans and environment. Effective removal of toxic heavy metals from aqueous solution is fundamental to the environment conservation and public health. The well-established toxicity of metals in solution sufficiently high concentrations affects humans, animals and vegetation [1–3]. Mercury, which is remarkably toxic and non-biodegradable, may reach the environment from a variety of sources, where it can be further converted into more toxic

forms [4]. Major sources of metals in the environment are waste-waters from industries like batteries manufacture, metal extraction, surface finishing and paints. Different processes such as ion exchange, reverse osmosis, adsorption, complexation and precipitation can be used for the removal of pollutants from aqueous media [5–7]. One known technique for removing heavy metals from wastewater is the using of natural adsorbents or sorption by materials based on natural substances. Many researchers are interested in adsorbing metal ions by chitosan, which is a biopolymer. Chitosan has been described as a suitable natural polymer for

the collection of metals ions, since the amino and hydroxyl groups on the chitosan chain act as chelating sites for metal ions. In the past, sorbents, which were prepared from natural organism like groundnut husks, bark, sunflower stalks, bagasse, rice, husk and sawdust, were used for removal of cadmium, chromium, copper, iron, nickel, lead and zinc [8–15]. These solids used for this sort of water decontamination are cation exchangers like resins and zeolites [16, 17]. The typical sorbents for mercury ions removal are activated carbons and zeolites [18–20]. The choice of adsorbent depends on the nature of pollutant. On the other hands, 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 [21–23].

The use of synthetic adsorber polymers in wastewater treatment has been investigated by several authors [24, 25]. 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 [26–28]. During the last few years, attempts were made to improve these adsorber polymers which originally were developed on the basis of ion exchange resins [29–32]. On the other hand, the use of new technologies allowed the production of highly porous polymers with a specific surface of  $800\text{--}1500\text{ m}^2\text{g}^{-1}$  which is similar to the surface of activated carbon [33].

The main objective of this work is to develop and application of seven synthetic polymers as potential sorbents for removal and determination of Hg(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.

## 2. EXPERIMENTAL

### 2.1 Reagents and Materials

Start materials were obtained as follows: dithizone (DTZ), poly(vinyl pyridine) (PVP), N,N'-methylenebis (acrylamide) (MBAAm-N,N'), poly(acrylamide) (PAAm), benzyl chloride and chloroform all from Merck or Fluka. The following inorganic materials were used:  $\text{Hg}(\text{NO}_3)_2$  (Merck), HCl 37% (Fluka). All solutions for experiments were prepared with distilled 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').

### 2.2 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 20 ml mercury solution (50 ppm) which contained certain amount of adsorbent and located on shaker at certain contact time and pH. Then the solution was filtered and 10 ml of DTZ solution (250 ppm in chloroform) was added to 10 ml of the filtrate. The most stable form of DTZ-Hg<sup>2+</sup> complex appear at pH=5.5, so DTZ must be added to the solution after adjusting pH to 5.5. The

absorbance of the solution was measured by a double-beam spectrophotometer. Because of the interference between DTZ-Hg complex and DTZ ligands, experiments were conducted at

595 nm, where the ligands have noticeable absorbance (Fig. 1). Standard solutions containing 1, 20, 50, 100, and 250 ppm Hg(II) were used for calibration.

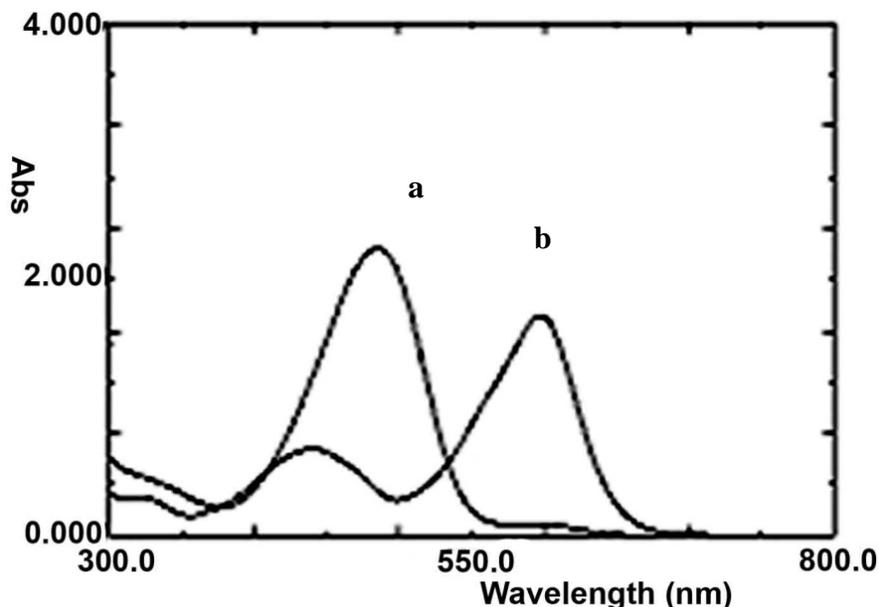


Fig. 1. Absorbance of Hg-DTZ complex (a) and DTZ (b) in chloroform solvent.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of pH on the Removal of Hg(II)

pH is an important parameter for removing metallic ions from solution, it has effect on the solubility of metallic ions, functional groups which exist on the adsorbent structure, concentration of the counter ions on the functional groups of the adsorbent and ionization degree of adsorbate. To examine the effect of pH on the Hg(II) removal efficiency, the pH of initial solution was adjusted to the corresponding pH value (0.5 – 6.5) using 0.1 M HCl. Fig. 2 shows effect of pH on removal of

mercury(II) ions from aqueous solution by these adsorbents. As shown in Fig. 2, the uptake of Hg(II) depends on pH, where optimum metal removal efficiency occurs at pH 6.5 for all studied polymers. As can be seen from Fig. 2, almost no adsorption of mercury(II) ions took place on synthetic polymers at  $\text{pH} < 1.5$ , probably due to the significant competitive adsorption of hydrogen ions. The adsorption studies at  $\text{pH} > 6.5$  were not conducted because of the precipitation of  $\text{Hg}(\text{OH})_2$  from the solution.

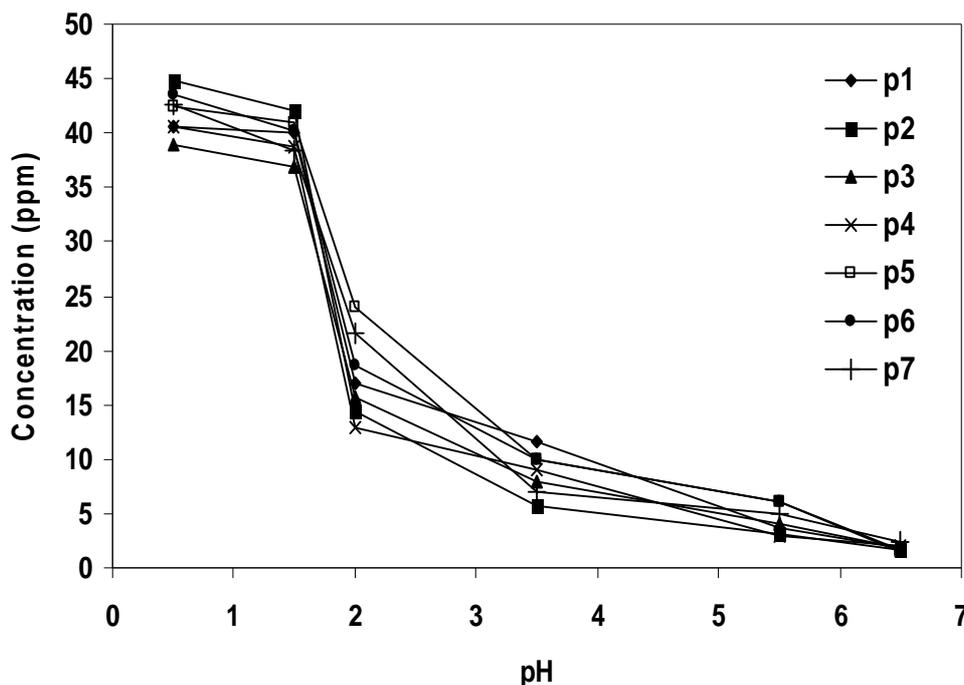
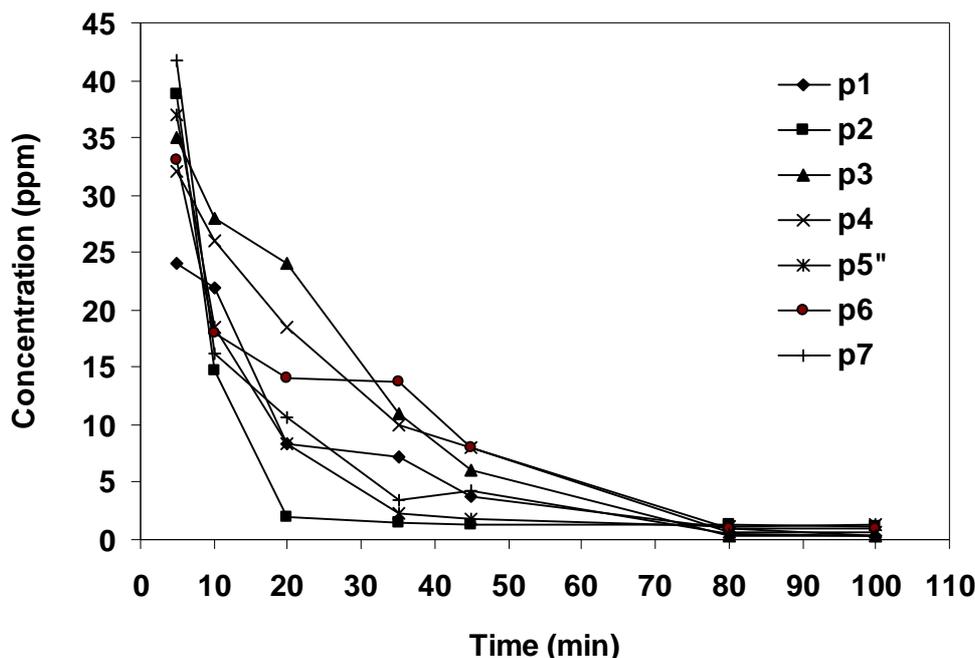


Fig. 2. Effect of pH on the Hg(II) removal efficiency using P1-P7 synthetic polymers.

### 3.2 Effect of contact time on the removal of Hg(II)

Before system reach to equilibrium state, increasing contact time between absorbent and Hg(II) solutions lead to growth the amount of absorbed ions. This result can be obtained if we consider constant value for other parameters like: absorbent dose which was used for experiments, and room temperature. As can be seen in Fig. 3, optimum agitation time for P2, P5 and

P1-P7 was found to be 20, 35 and 80 min, respectively. Greater availability of functional groups on the surface of polymers, which is required for interaction polymer and Hg(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 eco-nomical wastewater treatment system.

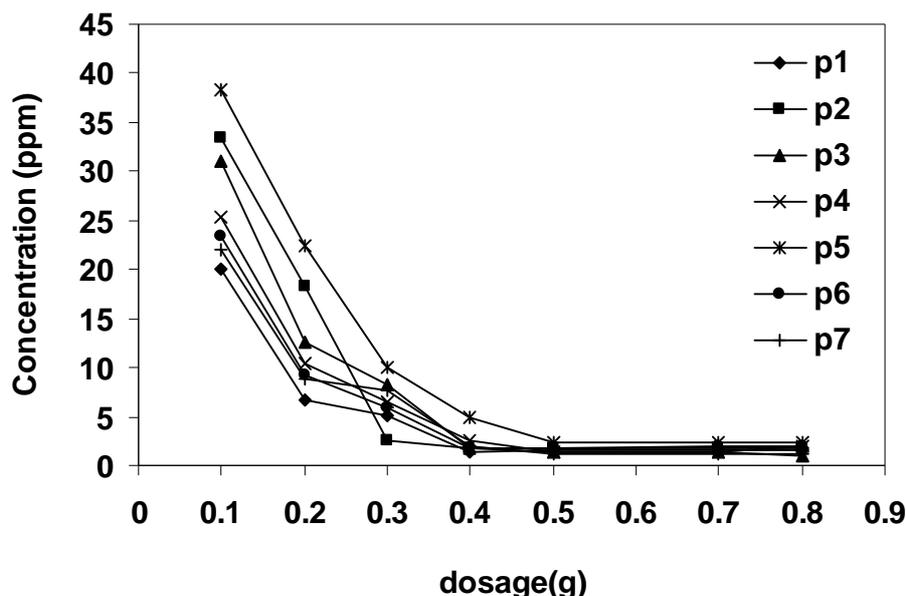


**Fig. 3.** Effect of agitation time on Hg(II) removal efficiency using P1-P7 synthetic polymers. Adsorbent dose: 0.3 g for P2, 0.4 g for P1, P3, P4, P6, P7 and 0.5 g for P5; pH 6.5.

### 3.3 Effect of Adsorbent Dose on Removal of Hg(II)

The dependence of Hg(II) sorption on adsorbent dosage was studied by varying the amount of polymers from 0.1 to 0.8 g, while keeping other parameters (pH and contact time) constant. Fig. 4 presents the Hg(II) removal efficiency for seven types of adsorbents used. Experiments showed that adsorbent dose rising led to an increase in the amount of removed ions, but this rising from 0.5 g to 0.8 g either couldn't change the value of removed ions or had a little effect on it. Furthermore, using high adsorbent dose

made problem in filtration processes of solution. 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 (0.3 g for P2, 0.4 g for P1, P3, P4, P6, P7 and 0.5 g for P5), the maximum adsorption sets in and hence the amount of Hg(II) bound to the adsorbent and the amount of Hg(II) in solution remains constant even with further addition of the dose of adsorbent.



**Fig. 4** The effect of sorbent dosage on Hg(II) removal efficiency using P1-P7 synthetic polymers. Agitation time: 20 min for P2, 35 min for P5 and 80 min for P1-P7; pH 6.5.

### 3.4 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 Hg(II) on the adsorbent

(mg/g),  $C_e$  the equilibrium Hg(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 Hg(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 Hg(II) using P1-P7 synthetic polymers.

Adsorbent type	Equation	Regression coefficient
P1	$\log q_e = 0.5359 \log C_e - 0.8229$	$R^2 = 0.9813$
P2	$\log q_e = 0.5612 \log C_e - 0.7268$	$R^2 = 0.9969$
P3	$\log q_e = 0.5925 \log C_e - 0.9154$	$R^2 = 0.9921$
P4	$\log q_e = 0.6032 \log C_e - 0.8232$	$R^2 = 0.9914$
P5	$\log q_e = 0.5897 \log C_e - 0.8201$	$R^2 = 0.9859$
P6	$\log q_e = 0.5125 \log C_e - 0.7942$	$R^2 = 0.9898$
P7	$\log q_e = 0.6198 \log C_e - 0.7759$	$R^2 = 0.9902$

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.

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

Adsorbent type	Equation	Regression coefficient
P1	$C_e/q_e = 0.0411 C_e + 4.7458$	$R^2 = 0.9920$
P2	$C_e/q_e = 0.0398 C_e + 4.7364$	$R^2 = 0.9964$
P3	$C_e/q_e = 0.0403 C_e + 4.8133$	$R^2 = 0.9911$
P4	$C_e/q_e = 0.0375 C_e + 4.7968$	$R^2 = 0.9885$
P5	$C_e/q_e = 0.0386 C_e + 4.8249$	$R^2 = 0.9928$
P6	$C_e/q_e = 0.0498 C_e + 4.8154$	$R^2 = 0.9846$
P7	$C_e/q_e = 0.0413 C_e + 4.7364$	$R^2 = 0.9919$

**Table 3.** Langmuir and Freundlich constants for the uptake of Hg(II) using P1-P7 synthetic polymers.

Adsorbent type	Freundlich constants		Langmuir constants	
	$n$	$k_f$ (L/mg)	$q_m$ (mg/g)	$b$ (L/mg)
P1	1.81	0.16	28.6	0.007
P2	1.91	0.17	43.4	0.008
P3	1.43	0.14	25.7	0.008
P4	1.59	0.17	29.3	0.008
P5	1.68	0.15	18.1	0.009
P6	1.76	0.17	22.4	0.009
P7	1.85	0.16	23.7	0.011

### 3.5 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 Hg(II) ions on all polymers tested at  $\text{pH} \leq 1.5$  was negligible. This suggested that desorption of mercury(II) ions

from these polymers was possible around pH 1.5. Therefore, HCl solutions of different pH (2.0, 1.5 and 0.5) were used to examine the desorption study. It was found that the desorption percentages were 83, 90, and 96% for P2 adsorbent in the HCl solutions of pH 2.0, 1.5, and 0.5, 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.

#### 4. CONCLUSION

Seven synthetic polymers were used for removal of Hg(II) ions from aqueous solutions. Based on the results, the P2 polymer was found as the best sorbent for adsorption of Hg(II) in shorter contact time (20 min) and lower amount of adsorbent (0.3 g). All polymeric sorbents showed significant pH dependence, which had a considerable effect on the mercury(II) removal. According to the collected results, the P2 polymer exhibited high performance as an adsorbent for removal of Hg(II) from aqueous solutions. Adsorption of Hg(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  $\leq 1.5$  was suitable for desorption of mercury(II) ions and the reusability of synthetic polymers were good.

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## مطالعات تجربی پیمانه‌ای حذف جیوه (II) از محلول‌های آبی توسط چند پلیمر سنتزی

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(تاریخ دریافت: خرداد 1392 - تاریخ پذیرش: مرداد 1392)

### چکیده:

در این تحقیق کاربرد تعدادی پلیمرهای سنتزی به عنوان جاذب برای حذف جیوه (II) از محلول‌های آبی مطالعه شده است. مطالعات تعادلی با روش معین در یک فرآیند پیمانه‌ای که در برگیرنده پارامترهای مختلفی مانند زمان بهم خوردن، مقدار جاذب و pH محلول آبی می‌باشد، انجام گردید. تغییرات غلظت جیوه (II) در محلول از طریق اندازه‌گیری مقدار کمپلکس DTZ-Hg(II) توسط طیف‌سنج دو پرتوی بررسی شده است. بخاطر تداخل جذبی کمپلکس DTZ-Hg(II) با لیگاندهای DTZ در 480 نانومتر که ماکزیمم طول موج کمپلکس می‌باشد، پیک جذبی در 595 نانومتر که متعلق به لیگاندهای DTZ می‌باشد، بررسی گردید. کاهش غلظت جیوه (II) بعد از تماس با جاذب‌ها، کارایی این جاذب‌ها را در استخراج جیوه (II) حتی در محلول‌هایی با غلظت بالای جیوه (II) را بیان می‌کند. در بررسی‌های جذب و واجذب مشاهده شد که پلیمرهای سنتزی وابستگی زیادی به pH نشان داده که کارایی حذف را به شدت تحت تاثیر قرار می‌دهد. رفتار جذب از ایزوترم‌های فروندلیچ ولانگمویر تبعیت می‌کند. مطالعه بازیابی نیز انجام شده است.

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