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Mercury Uptake Capacity of Chitosan: Kinetic and Isotherm Study

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IN this study, the ability of chitosan (β (1→4) linkage of 2-acetamido-2-deoxy-β-D glucose] to remove mercury from water samples was studied. Chitosan was characterized by FT-IR, XRD and FE-SEM. The Hg (II) uptake capacity was studied; different factors were considered such as pH, contact time, adsorbent dose, metal ion concentration. From the obtained results, it was found that chitosan exhibited a maximum uptake capacity of 32.83 mg/g under the investigated conditions. The uptake process was found to follow Frundlish Adsorption Isotherm and Pseudo Second Order Kinetics.

Mercury (Hg) is a highly toxic metal that contaminates our water and air supplies. Approximately two thirds of the Hg in natural environments is of anthropogenic origin(1) . Burning of fossil fuels, such as petroleum, natural gas and coal, is the most important contributor to the total environmental Hg budget, since they contain approximately 0.2 ppm of Hg(2) . Mercury can be found in significant amounts in wastes from chlor-alkali manufacturing plants, electrical and electronics manufacturing, and sulfide ore roasting operations. Exposure to Hg can have toxic effects on reproduction, the central nervous system, liver, and kidneys, and causes sensory and psychological impairments.

The deposition and discharge of Hg into natural waters have resulted in Hg concentrations greater than 0.5 μg/g wet weight in many species of freshwater fish throughout the US(3) . More fish consumption advisories resulting from mercury have been issued by state health agencies than for all other contaminants combined. In the US, as of 1999, 41 states had issued Hg-related human health advisories for fish consumption, up from 27 states in 1993. Mercury in industrial effluents and flue gas is usually recovered using chelating agents, which are not reusable after Hg is removed by distillation(4) . Alternative treatment methods are greatly needed to keep Hg out of the environment.

In order to minimize the adverse effects of Hg in the environment, it is desirable to find ways to capture it before it becomes a problem. Several techniques are available for this including precipitation, ion exchange and adsorption. Precipitation is effective within a narrow pH range and results in large volumes of Hg-containing sludge, while ion exchange is effective only for wastes with low dissolved solids concentrations. Adsorbents can be designed that are specific to Hg and whose volume is much less than an amorphous sludge. Bailey *et al*.(5) reviewed several adsorbents and their applications for Hg removal and found that several natural materials were capable of adsorbing moderately high amounts of Hg.

Chitin (poly(D-acetylglucosamine)) and chitosan (poly(D-glucosamine)) are natural polysaccharides found in fungi. Chitosan is also produced by deacetylation of chitin that is found in the shells of crustaceans(6) . Shellfish waste represents the source of most commercially available chitosan. Chitosan has found a great many uses in a wide variety of fields. It can be used as a protective coating on food and seeds, to clarify suspensions by coagulation, to capture and reclaim metals or proteins, and to serve as a time-release structure for medicines (7,8) .

Chitin and chitosan have been investigated as adsorbents for metal removal by researchers worldwide. Due to their high nitrogen content and porosity, chitosan-based sorbents have exhibited relatively high sorption capacities and kinetics for most heavy metals(9) .

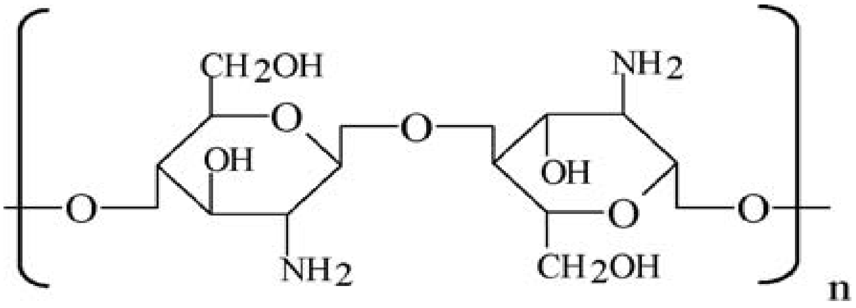

Fig. 1. Molecular structure of chitosan.

In this paper the removal of mercury ions from waste water using chitosan as adsorbent materials was investigated. The uptake of mercury ions for Cs. from aqueous solutions was studied at different parameters including time, adsorbent dose, metal ion concentration and pH. Also, the adsorption isotherm and kinetics were studied.

Materials and Methods

Chitosan was purchased from Sigma-Aldrich company. Mercury II standard solution was purchased from Merck company, Germany. All other reagents were high grade and used as received without further purification. Deionized water was used to prepare all solutions. Solutions were prepared and stored in glass containers. Glass was cleaned in dilute HNO_3 (10% v/v) and then dried at 60˚C after rinsing with deionized water.

Characterization of chitosan

The FT-IR spectra were recorded on a Nicolet Is-10 FT-IR thermo fisher scientific spectrometer. The samples were characterized by X-ray diffraction (XRD) using a Philips X'Pertpro Pan-analytical instrument. The data were taken for the 2θ range of 0 to 80 degrees with a step of 0.02 degree. The Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained using Quanta FEG 250, FEI Co, Netherlands.

Adsorption studies

Different concentrations of mercury were prepared by dilution of 1000 ppm standard stock solution using deionized water. A wide concentrations range (0.02 to 100 ppm) was studied. Batch-mode adsorption studies were carried out by taking 20 ml of the desired mercury (II) solutions in 50 ml flasks. The pH was adjusted to the desired value using a pH meter (model Mettler – Tolledo AG, Switzerland).

A known weight of the polymer was added to the flasks and the mixture was agitated in a water bath shaker at 300 rpm for pre-determined time intervals. Then, the adsorbent was removed from the solution using filter paper and the aqueous solution was analyzed for mercury concentration using cold vapor atomic absorption spectrometer (CV-AAS) based on a hydride system. It has been used for the quantitative determination of mercury in liquid samples due to its high sensitivity and selectivity as well as extremely low detection limit (1 μg/L). This technique uses $NaBH_4$ to reduce Hg in presence of argon as a carrier gas and moved through a gas liquid separator, then the gaseous mercury is enriched on a gold collector then carried out to a quartz cell where the elemental mercury concentration is measured .All experiments were measured in triplicate and average values were used in the graphs.

Various parameters such as effect of metal ion concentration, weight of the adsorbent, pH of the media and contact time, were studied to evaluate the uptake capacity, efficiency and selectivity of Cs.

Uptake capacity of Cs. can be calculated from the following equation:

$$\text{Uptake capacity (mg/g)} = (C_o\text{-}C_a).\text{Vol./ wt.} \quad (1)$$

While adsorption efficiency was obtained as follows:

$$\text{Uptake efficiency (\%)} = [(C_o\text{-}C_a) \times 100] / C_o \quad (2)$$

where: C_o: initial concentration, C_a: remaining concentration after treatment, V: volume of pollutant to be treated in liter, wt.: weight of adsorbent in gram.

Effect of contact time

In order to evaluate kinetic data, the initial Hg concentration (100 mg/L), solution pH (7.0) and adsorbent concentration (2 g/L) were kept constant. Samples were taken at each predetermined time for the analysis of residual metal concentration in solution.

Effect of adsorbent concentration

The effect of adsorbent concentration on the adsorption of Hg was studied in the range of 0.5 g/L to 2 g/ L. Solution pH was maintained constant at 7.0, the initial Hg concentration was 100 mg/L and the contact time was 1hr.

Effect of the initial mercury ions concentration

The effect of the initial Hg ions concentration was studied at different concentrations of metal ions (from 0.02 to100 mg/L). Solution pH (7.0), contact time of 1hr and adsorbent concentration (2 g/L) were kept constant.

Effect of pH

The effect of pH on the adsorption rates of the prepared composites with Hg(II) was investigated in pH range 5.0–9.0 (which was adjusted with HNO_3 or NaOH at the beginning of the experiment). All other parameters were kept constant; the initial Hg concentration (C_0) was 100 mg/L, The adsorbent concentration was 2 g/ L, and the contact time was 1hr.

Results and Discussion

Characterization of adsorbent

In order to fully characterise the materials, a spectrum of pure chitosan was recorded (Fig. 2). The main bands appearing in the spectrum of chitosan (CS) powder are due to stretching vibrations of OH groups in the range from 3750 cm^{-1} to 3000 cm^{-1} and C–H bond in $-CH_2$ ($\nu_1 = 2930\ cm^{-1}$) and $-CH_3$($\nu_2 = 2875\ cm^{-1}$) groups, respectively. The range of 1680–1480 cm^{-1} was related to the vibrations of carbonyl bonds (C═O) of amide group CONHR (secondary amide, $\nu_1 = 1660\ cm^{-1}$) and to the vibrations of amine group NH_2, $\nu_2 = 1580\ cm^{-1}$. The spectra in the range from 1160 cm^{-1} to 1000 cm^{-1}have been analysed by many authors who attribute vibrations appearing in this range to CO group(10,11) . The band located near $\nu = 1150\ cm^{-1}$ is related to asymmetric vibrations of CO in oxygen bridge resulting from deacetylation of chitosan(12) .

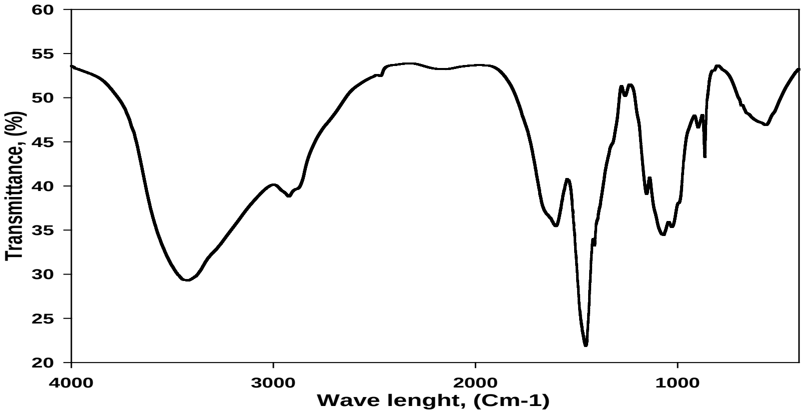

Fig. 2. IR spectrum of Cs.

The X-ray diffraction pattern of chitosan shows a high intensity beak at 2θ=20^o. The peak corresponds to the amorphous structure of chitosan$^{(13)}$.

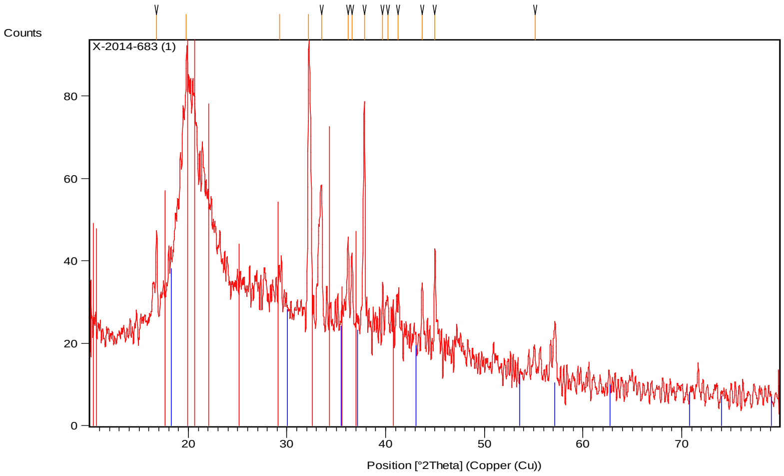

Fig. 3. XRD pattern of Cs.

Morpology

The morphology of the surface was monitored using scanning electron microscope. Figure 4 shows that chitosan surface is inert, homogenous and smooth without pores or shrinkage.

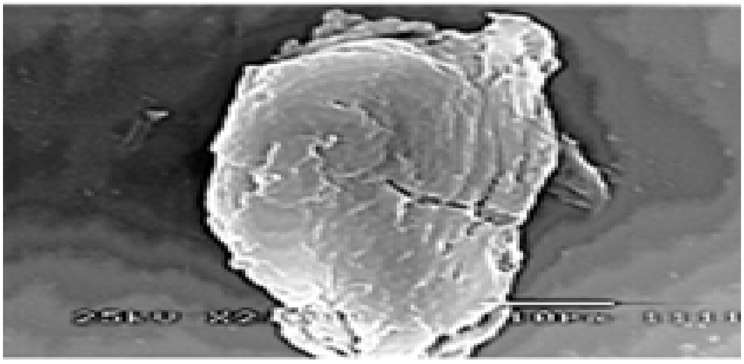

Fig. 4. SEM images of Cs.

Adsorption studies

Chitosan is a biopolymer that contains a multi-site of chelation for heavy metals such as –OH, -CH_2OH and the –NH_2group which can bind with the metal ion through the lone pair of electron in the nitrogen atom. This makes chitosan have a high uptake capacity compared to other adsorbents.

Effect of contact time & adsorption kinetics

The adsorption behavior of Hg (II) on Cs. at initial concentration of 100 ppm, pH 7.0 using adsorbent dosage of 2g/l as a function of contacting time was shown in Fig. 5.

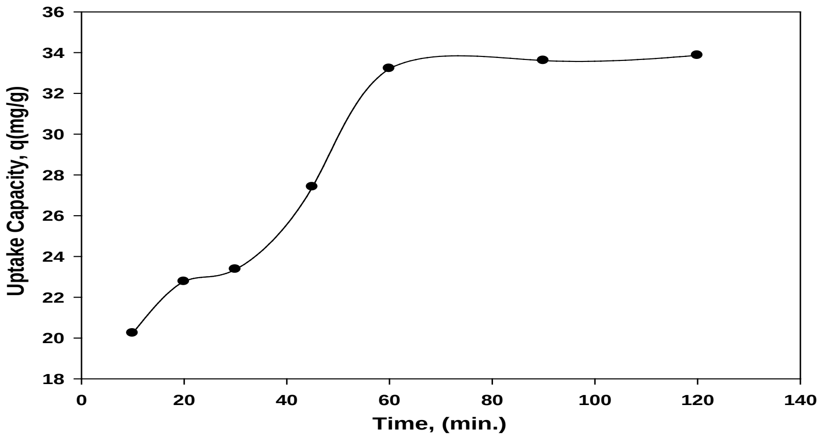

Fig. 5. Effect of contact time on Hg (II) uptake capacity of Cs.

It could be seen that the adsorption rate of Hg (II) on the prepared materials was initially quite high and then gradually reached equilibrium within 60 min.

In order to determine the adsorption mechanism of Hg ions onto chitosan, four kinetic models were applied to fit the experimental data; first order, second order, pseudo-first-order and the pseudo-second-order models.

The pseudo-first order kinetic model was suggested by Lagergren(14) for the adsorption of solid/liquid systems and its linear form can be formulated as:

$$Ln(qe - qt) = \frac{Ln(qe) - K_{1p}\,t}{2.303} \qquad (3)$$

The 1st order kinetic model linear form can be formulated as:

$$Log\,\frac{qe - qt}{qe} = \frac{K1t}{2.303} \qquad (4)$$

Ho and McKay's pseudo-second order kinetic model[i] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{2kq^2{}_e} + \frac{t}{q_e} \qquad (5)$$

The 2nd order kinetic model linear form can be formulated as:

$$\frac{1}{q_{e}-q_{t}} = \frac{1}{q_{e}} + k_{p2}t \qquad (6)$$

where q_e and q_t are the amount of M (II) adsorbed at equilibrium (mg/g) and time t, respectively. k_{1p} is the equilibrium rate constant of the pseudo-first order adsorption (min^{-1}). k_1 is the equilibrium rate constant of the first order adsorption (min^{-1}). k_{2p} is the equilibrium rate constant of the pseudo-second order adsorption (g/mg.min). k_2 is the equilibrium rate constant of the second order adsorption (1/g.mg.min).

The calculated kinetics parameters for chitosan are listed in Table 1. As can be observed, the correlation coefficients (R^2) of the pseudo-second-order kinetics model are higher than those of the pseudo-first-order kinetics model.

TABLE 1. Kinetic model rate constants for adsorption of Hg (II) on the prepared composites.

Pseudo 1*st* order		**1*st* order**		**Pseudo 2*nd* order**			**2*nd* order**	
R^2	**K_{p1}**	**R^2**	**K_1**	**R^2**	**q_e**	**K_{p2}**	**R^2**	**K_2**
0.8388	0.0152	0.8388	-0.5299	0.9903	37.88	0.002014	0.8654	0.0021

The consistency of the experimental data with the pseudo-second-order kinetic model, as shown in Fig. 6, indicates that the adsorption of Hg (II) on chitosan is controlled by chemical adsorption (chemisorption) involving valence forces through sharing or exchange electrons between sorbent and sorbate. In the chemical adsorption, it is assumed that, the adsorption capacity is proportional to the number of active sites occupied on the adsorbent surface(16).

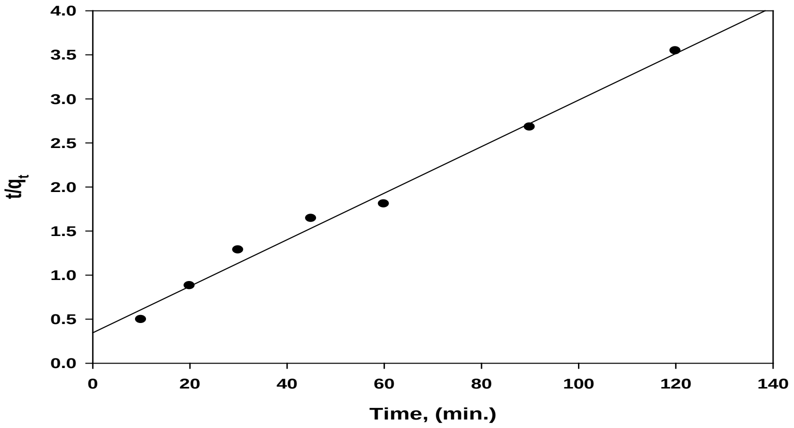

Fig. 6. Pseudo 2*nd* order kinetic model for the adsorption of Hg (II) on Cs.

Effect of adsorpent dose

The effect of adsorbent dose on adsorption was examined by operating various dosages; 0.5 g/L, 1 g/L and 2 g/L of chitosan of 100 ppm of metal solutions at room temperature. Figure 7 shows that as the dosage increased, the percentage of removal ions increased as well due to the greater availability of adsorption sites for Hg ions. It is noticed that at adsorbent conc. equal to 2 g/L, the uptake efficiency reaches about 64% of mercury ion removal for chitosan.

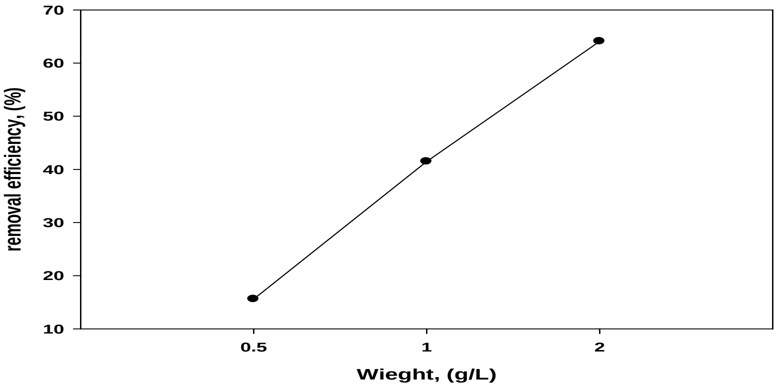

Fig. 7. Effect of adsorption dose on the Hg (II) uptake efficiency of Cs.

Effect of Hg (II) ions concentration & the adsorption isotherms

The effect of concentration of mercury ions was examined by studying different concentrations varying from 20 ppb to 100 ppm as shown in Fig. 8. The adsorbent dosage used was 2 g/L. The maximum capacity reached is 32.7 mg/g and the uptake capacity increased with the increase of concentration. The increased number of the metal ions in the solution increases the opportunity of the active group to bind with the metal ion which increase the uptake efficiency.

Four models of adsorption isotherms were studied to describe the adsorption isotherms of Hg (II) by chitosan (Langmuire, Freundlich, Tempkin and D-R model) (Fig.9), Freundlich equation was found to have the highest correlation factor, which are expressed as follows:

$$\text{Log}q_e = \log K_F + 1/n \log C_e \qquad (7)$$

where C_e(mg/L) is the equilibrium concentration of Hg(II), q_e (mg/L) is the amount adsorbed under equilibrium, K_F and n are the Freundlich empirical constants.

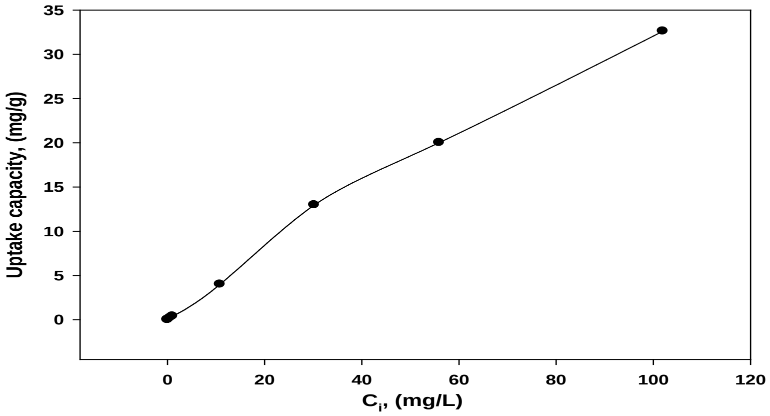

Fig. 8. Effect of Hg (II) ions concentration on the uptake capacity of chitosan.

As shown in Fig. 9, the correlation coefficient (R^2) is high, the existence of heterogeneous adsorption sites is approved which may be attributed to the presence of many sites of adsorption for mercury ions.

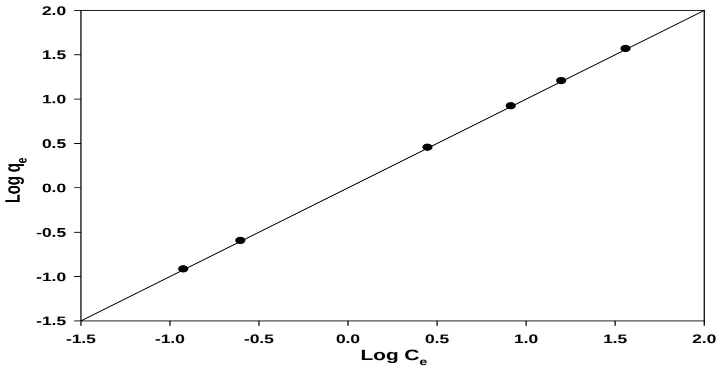

Fig. 9. Freundlich adsorption isotherm for Hg(II) adsorption on Cs.

Effect of Hg (II) ions solution pH

Hg (II) removal by Cs. was measured in batch systems with pH values from 5 to 9 as shown in Fig.10. The adsorption of mercury ions was higher at pH 5 and decreased sharply untill reaches the pH of 9. The highest adsorption values were achieved at pH 5 for mercury ions with the sorbents. The pH values less than 5 were avoided due to the solubility of chitosan in low pH values, while the pH values were also avoided due to the possibility of precipitation of Hg^{2+} ions in the solution as hydroxides.

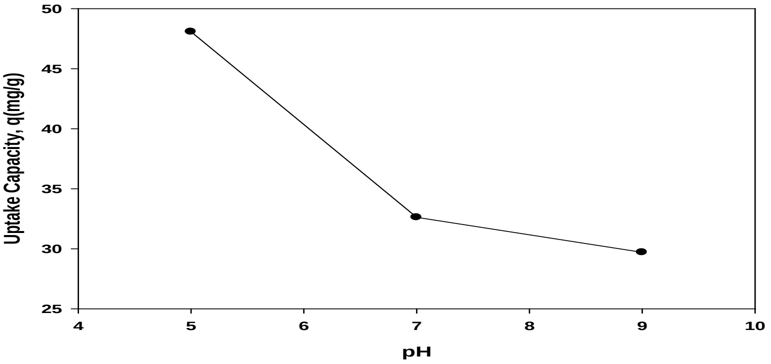

Fig. 10. Effect of Hg (II) ions solution pH on the uptake efficiency of Cs.

Conclusion

Chitosan, the second most abundant natural polymer after cellulose, has a unique chemical structure rich in amino- and hydroxide groups which allow it to be used as an adsorbent for toxic heavy metal. In Addition, the biodegradability and biocompetability of chitosan make it an echo-friendly candidate that will not cause additional environmental problems upon using in water treatment.

The uptake capacity of mercury, as one of the most toxic heavy metals, using chitosan was studied. The maximum mercury ions uptake was 32 mg/g within the investigated conditions. The uptake process was found to follows Frundlish adsorption isotherm and pseudo second order kinetics.

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سعة إمتصاص الزئبق من المياه بإستخدام الكيتوزان : دراسة ميكانيكية

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فى هذا البحث تمت دراسة قدرة الكيتوزان على امتصاص الزئبق من مياه الصرف الصناعى . فتم توصيف المركب باستخدام العديد من أجهزة التوصيف والتحليل مثل جهاز حيود الأشعة السينية واستخدام أيضا الاشعة تحت الحمراء وتصويره بالميكروسكوب الالكترونى الماسح. أثبتت النتائج ان قدرة الكيتوزان على 3 امتصاص الزئبق تصل الى 32 مجرام/جرام. وبالتالى يمكن تطبيقه فى المصارف الصناعيه التى تعانى من زيادة نسبه الزئبق بالمياه.