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Adsorption study on chitosan: Removal of copper (II), mercury (II) and chomium (III) adsorption from aqueous solution

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ABSTRACT

The adsorption of Copper (II), Mercury (II) and Chromium (III) on chitosan has been studied in batch mode using flame atomic absorption spectroscopy for metal estimation. The maximum amounts of Copper (II), Mercury (II) and Chromium (III), adsorbed (qm), as evaluated by Langmuir isotherm, were 14.81 mg 14.01 mg and 9.65 per gram of powder of chitosan, respectively. The negative values of Gibb's free energy change ($\Delta G°$) showed that the adsorption process was feasible and spontaneous in nature.

KEYWORDS

Langmuir isotherm;
Freundlich isotherm;
Heavy metals;
Chitosan;
Pontaneous.

INTRODUCTION

Heavy metal pollution has become an environmental problem throughout the world because heavy metals can be accumulated into the food chain and cause serious problems, not only for ecosystems but also for human health. The selective removal of industrial heavy metals from liquid waste is consequently the subject of considerable ecological and economic interest[1]. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. wastes containing soluble toxic heavy metals requires concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrices[2].

Mercury (Hg) emissions from waste incineration are a global problem, indicated by that nearly half of the Hg emissions reaching the Arctic originates from waste incineration[3]. In most countries, the total Hg emissions from waste incineration are largely underestimated because of poor knowledge about Hg content in wastes and due to economic reasons there are no or only limited analyses available on Hg content in flue gases from a majority of the waste incineration plants in operation[4].

Chromium (Cr) compounds are widely used by many modern industries such as leather tanning, electroplating, metal finishing, paint and pigments, resulting in a large quantity of this element being discharged into effluent industrial wastewaters. Waters containing a high concentration of Cr can cause serious environmental problems as well as induce toxic and carcinogenic health effects on humans[5]. Therefore, the removal of Cr from wastewaters arouses great attention.

Copper (Cu) has been known as one of the most common toxic metals, which finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the nonferrous metal industry, the printing and photographic industries and metal working and finishing processes[7-8]. as a metal provides limited scope for environmental pollution, but the waste generated by copper-based industries with various toxic elements can pollute the environment. Copper mining, smelting, and refining activities are often associated with the generation of a large quantity of wastes. Overburden, mine tailings, sediment from concentrator plants and scrap, slag, dross, slime, flue dust, mill scales, and sludge from the process are the major sources of pollution unless handled and treated suitably[8-9].

Chitin and chitosan are of commercial interest due to their high percentage of nitrogen (6.9%). Amine and hydroxyl groups on their chemical structures act as chelation sites for metal ions making them useful chelating agent. Chitin and chitosan are considered as natural polymers which have excellent properties such as biocompatibility, biodegradability, non-toxicity, metal adsorption, etc[10]. A recent study by Dambies et al[11] showed that chitosan beads removed about 60% of Cr (VI) ions from aqueous solution. Ngah et al[12] and Gyliene et al[13] stated that chitosan could be effective adsorbent for collection of Cu (II) ions from aqueous solutions.

The goal of this study was to investigate the extent of removal of contaminant heavy-metal species (Cu, Hg and Cr) from aqueous Solution by chitosan. Maximum adsorption capacity of adsorbent, adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were estimated by Langmuir and Freundlich isotherms, respectively.

EXPERIMENTAL

High-molecular weight chitosan from crab shells with ~ 81% degree of deacetylation and an average molecular weight of approximately 880 kDa according to manufacturers specification was obtained from Aldrich Chemical Co. Cu (II) stock solution was prepared by dissolving 1 g of Cu (II) metal in 50 ml of 5 M nitric acid before diluted to 1 L volume with deionised water. Standard solution of Cr (III) was prepared by dissolving 7.6960 g Cr (NO3)3·9H2O (reagent grade from Merck, Darmstadt, Germany) in 250 mL deionized water and diluting to 1 L adding HNO3 to obtain a final concentration of 2% (v/v); this was checked against a titrisol standard solution from Merck (Darmstadt, Germany). The Hg (II) stock solution was prepared by dissolving 1 g of 5 M nitric acid prior to dilution with deionised water to 1 L volume. Standard solutions of the desired concentrations (10–100 μgmL^{-1}) were prepared by successive dilutions of the corresponding stock solutions. The pH was adjusted using 0.1 M HCl and NaOH solutions.

Equipment and apparatus

pH adjustments were made with digital pH-meter (Sartorius, Model PP-20) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Mercury, *Copper* and Chromium content in each experiment were determined with flame atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100).

Adsorption isotherms

The adsorption isotherms were obtained by employing 100 mg of chitosan and 25 mL of Waste solution with different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μg mL^{-1}). These solutions were stirred in a mechanical shaker until they reached adsorption equilibrium. The system was shaken for 90 min and then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry.

pH optimization

The removal of Hg (II), Cu (II) and Cr (III) at different pH was studied in batch mode. A 25-ml of test solution of fixed concentrations was treated with 0.3 g of chitosan and agitated intermittently for 45 min. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in 45 min. After this period the solution then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry. The metal concentration retained in the sorbent phase (q_e, mg/g) was calculated by using Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (M), *V* the solution volume (l) and *m* is the mass of chitosan (g).

Equilibrium modeling in a batch system

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure. The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium for water and wastewater treatment applications.

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The adsorption curves were applied to both the Langmuir and Freundlich equations. The Freundlich isotherm model, which assumes that the adsorption occurs on heterogeneous surfaces, is often expressed as;

$$q_e = K_f (C_e)^{1/n} \tag{2}$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{3}$$

where K_f is Freundlich isotherm constant (L/g) and n_F is Freundlich isotherm exponent. Values of K_F and n_F were calculated from the intercept and slope of plots ln q_e vs ln C_e and a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The value of n_F should be greater than one confirming good adsorption of heavy metals onto chitosan. Langmuir isotherm, which assume that a monolayer of heavy metals is formed on a relatively regular adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir isotherm has been successfully applied to many real sorption processes and is expressed as follows:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \tag{4}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), b a constant related to the energy or net enthalpy of adsorption (L/mg), and Q_0 the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g). Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with heavy metals and allows the comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiments[14]. The Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \tag{5}$$

By plotting (C_e/q_e) versus C_e, Q^0 and b can be determined if a straight line is obtained. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where b is the Langmuir constant and C_0 the initial heavy metals concentration (mg/L). R_L value indicates the type of isotherm. According to[14], R_L values between 0 and 1 indicate favorable adsorption.

RESULTS AND DISCUSSION

The adsorption kinetics is influenced by various factors, which include initial heavy metals concentration, amount of adsorbent and time. The initial heavy metals concentration is one of the most important factors that determines the equilibrium concentration, but also determines the uptake rate of heavy metals and the kinetic character.

Effect of heavy metals concentration on adsorption

Figure 1 shows equilibrium adsorption isotherm of Hg (II), Cu (II) and Cr (III) on chitosan at 298 ÚK. The equilibrium adsorption density q_e is increased with the increase in Hg (II), Cu (II) and Cr (III) concentration. At low equilibrium heavy metals concentrations C_e, the equilibrium adsorption densities q_e of the chitosan reach almost the same q_e as those at high equilibrium Hg (II), Cu (II) and Cr (III) concentrations. It indicates that chitosan have high adsorption density even at low equilibrium Hg (II), Cu (II) and Cr (III) concentrations.

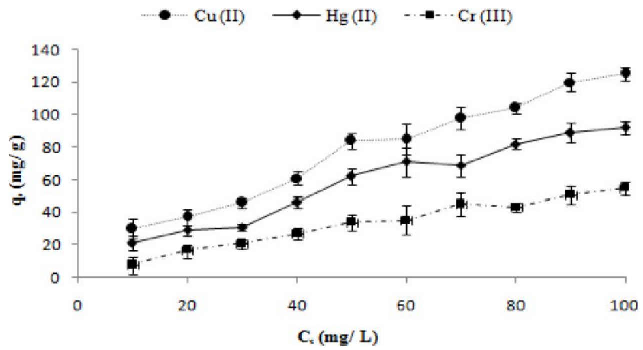

Figure 1 : Equilibrium adsorption isotherm of of Cu (II), Hg (II) and Cr (III) on chitosan

Figure 1 shows the effect of heavy metals concentration on chitosan adsorption. An increase in initial concentration of heavy metals led to an increase in the adsorption capacity of heavy metals on chitosan. This indicates that the initial concentration of heavy metals played an important role in the adsorption capacity of heavy metals on heavy metals. The dotted lines in Figures 2 and 3 represent a linear regression fit to the results for both isotherms. However, since adsorption data are of a nonlinear nature, nonlinear regressions are also performed on each set of data points. These nonlinear regression fits are represented as solid lines in Figures 2 and 3.

The correlation coefficients obtained with both kinds

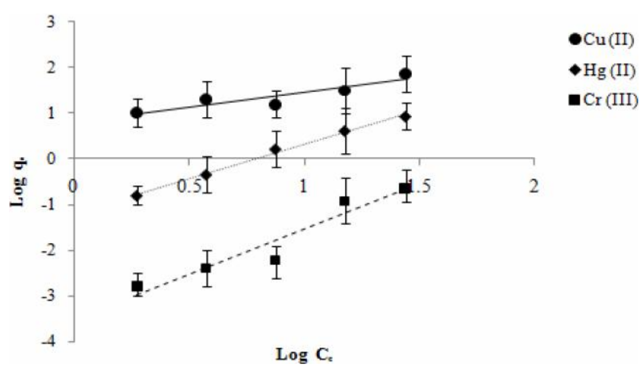

Figure 2 : Freundlich adsorption isotherm at 298 ^{0}K.

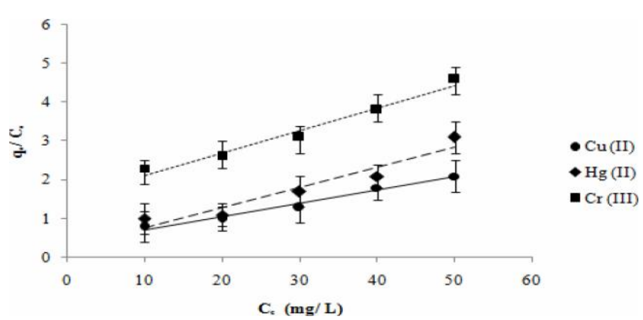

Figure 3 : Langmuir adsorption isotherm at 298 ^{0}K.

of regression for both adsorption isotherms are summarized in TABLE 1. The correlation coefficient values in TABLE 1 indicate that the data fit the Langmuir isotherm better than the Freundlich isotherm, both in case of linear and nonlinear regression.

Effect of pH

To study the effect of pH on adsorption, experiments were carried out in the pH range 1–9 for Hg (II), Cu (II) and Cr (III). Figure 4 shows that the removal of metal ions was increased with increasing initial pH of metal ion solution and maximum value was reached at pH 4 for Cr (III), 5 for Hg (II) and 5-6 for Cu (II).

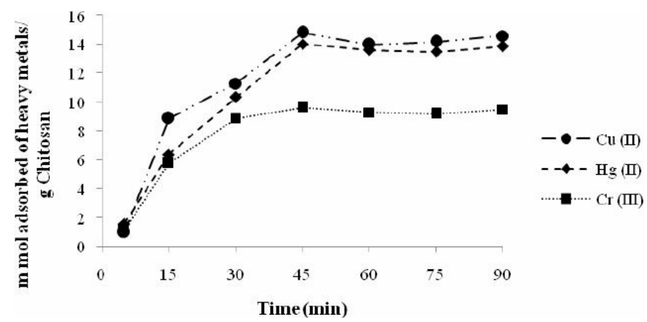

Figure 4 : Adsorption rate of Cu (II), Hg (II) and Cr (III) by chitosan from aqueous solutions: Adsorption conditions; initial concentration of heavy metals: 20 mg/L, amount of chitosan: 0.3 g, volume of adsorption medium: 25 mL, temperature: 298 ^{0}K.

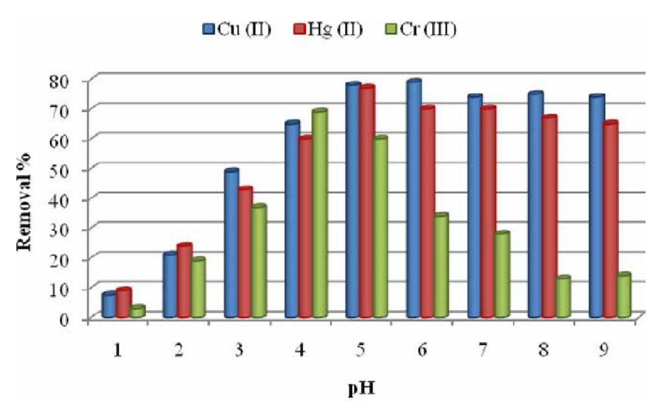

Figure 5 : Effect of pH on adsorption of Cu (II), Hg (II) and Cr (III) on chitosan.

Changes of free energy

The effect of temperature on the adsorption of heavy metals on chitosan was investigated by conducting experiments for 30 mg/L of initial metals ion concentrations at 298, 303, 308, 313, and 318 °K. It was observed that on increasing the temperature percentage removal of heavy metals increased. This showed that the adsorption process was endothermic in nature.

The thermodynamic parameters Gibb's free energy ($\Delta G°$), enthalpy (ΔH) and entropy ($\Delta S°$) were calculated using the following equations:

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^o}{R} + \frac{-\Delta H^o}{RT} \quad (7)$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \quad (8)$$

where m is the adsorbent dose (g/L), C_e is concentration of metals ion (mg/L), q_e is the amount of metals ion at equilibrium in unit mass of adsorbent (mg/g), q_e/C_e is called the adsorption affinity. ΔH, $\Delta S°$ and $\Delta G°$ are change in enthalpy (kJ/mol), entropy (J/(mol K)) and free energy (kJ/mol), respectively. R is the gas constant (8.314 J/mol/K) and T is the temperature (K).

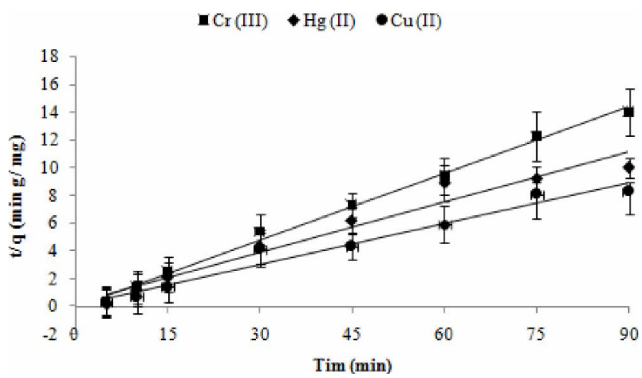

Figure 6 : Pseudo-second-order kinetic model fitting for Cu (II), Hg (II) and Cr (III) adsorption on chitosan.

The values of ΔH and $\Delta S°$ were obtained from the slopes and intercepts of the Van't Hoff plots of ln ($q_e m/C_e$) vs. 1/T, respectively, thereafter $\Delta G°$ values were determined from Eq. (7). The values of thermodynamic parameters are presented in TABLE 2. The results showed that the $\Delta G°$ values are negative and increased in their absolute values with temperature. This result suggested that a high temperature is favoured for the adsorption of heavy metals on chitosan, indicated a spontaneous adsorption process. The values of heat of adsorption, ΔH is positive for metals ion, indicated that the adsorption process of heavy metals on chitosan was endothermic. A positive ΔS suggested that heavy metals were not stable on the adsorption sites of chitosan probably due to the increase in translational energy of metals ion.

TABLE 2 : Thermodynamic parameters for adsorption of Cu (II), Hg (II) and Cr (III) on chitosan.

Meta ions	*ΔH° (kJ/mol)*	*ΔS° (Jmol/K)*	*-ΔG°(kJ/mol)*				
			298 °K	303 °K	308 °K	313 °K	318 °K
Cu (II)	84.235	309.913	8.119	9.668	11.218	12.767	14.317
Hg (II)	64.498	239.138	6.762	7.957	9.153	10.349	11.544
Cr (III)	32.426	117.776	2.671	3.26	3.849	4.437	5.026

CONCLUSIONS

The current study emphasizes on the ability of chitosan to adsorb heavy metals from aqueous solutions. In batch mode studies the adsorption was dependent on initial metals ion concentration and agitation time. The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm for metals ion studied. Although the adsorptive capacity of chitosan is not excessively. high for heavy metals, low cost of the material together with its adsorptive ability could offer a promising procedure for depollution of industrial wastewaters. The negative values of $\Delta G°$ suggested that the adsorption was spontaneous in nature. The positive value of ΔH and ΔS indicated endothermic adsorption process and increased randomness at surface–solution interface, respectively.

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