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Kinetic study and modeling of Zn^{2+}removal from wastewater by adsorption onto multi-walled carbon nanotubes

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Adsorption methods for the removal of Zn^{2+} as a toxic heavy metal ion using multi-walled carbon nanotubes (MWCNTs) as an adsorbent are presented here. SEM and FTIR techniques were used for the characterization of the MWCNTs. The relationship between the optimization factors (adsorbent dosage, contact time and initial heavy metal ion concentration) and the adsorption properties of the MWCNTs was studied. The quantity of metals adsorbed during various time intervals is the base of kinetics of adsorption. A thorough investigation was done on the modeling of kinetic curves. The results of the adsorption kinetics study showed that the adsorption of Zn^{2+} fitted most closely to the pseudo-second-order model (R^2>0.999), and the adsorption equilibrium time was 55 min. The Langmuir isotherm model was used to fit the adsorption equilibrium data.

Keywords: Multi-walled carbon nanotubes; Adsorption; Kinetics; Isotherm; Zn^{2+}, Water treatment.

INTRODUCTION

Heavy metals are nowadays among the most important pollutants in surface and groundwater [1, 2]. Thus, the removal of such toxic materials from wastewater is becoming a crucial issue. To control this issue, many physical, chemical and biological technologies have been developed [3, 4]. Due to its high efficiency and economic consideration, adsorption process was reported to be the most suitable method to this purpose [5, 6]. In addition, adsorption does not result in secondary pollution by producing harmful substances during the process [7-10]. Some adsorbents such as zeolites, biomaterials, polymers, etc., have been extensively used for adsorption of toxic heavy metal ions [11-16]. Since the adsorption efficiency is mostly dependent on the adsorbent properties, therefore developing an effective adsorbent is of vital importance for the widely applications of adsorption in water treatment [17-19]. Therefore, development of more efficient adsorbents has attracted the attention of quite a large number of researchers. New adsorbents based on nanomaterials are used to remove heavy metal ions from wastewater and remove the traditional sorbents defects [20, 21]. Carbon nanotubes (CNTs) have attracted significant interdisciplinary interest on account of their exclusive physical and chemical properties; nonetheless, the hydrophobicity of CNTs may restrict some of their applications [22, 23]. Therefore, CNTs surface treatments with functional groups or nanoparticles leads to overcoming of their drawbacks toward some applications [24-27]. The aim of the present paper was to study the possibility of the removal of Zn^{2+} heavy metal ions by MWCNTs. A kinetic study according to three different models was applied. The reaction order and the rate constants were studied and calculated using batch studies.

EXPERIMENTAL

Materials

MWCNTs were obtained from NanoAmor Nanostructured & Amorphous Materials, Inc, USA. Chemical vapor deposition (CVD) method was used to prepare MWCNTs with purity of 95%, outer diameters of 50 nm, length in the range from 500 to 2000 nm and specific surface area of 40 m^2 g^{-1}. In addition, $ZnCl_2$ aqueous solutions with different concentrations were prepared and used as sources of Zn^{2+}. All other chemicals were purchased from Merck Inc, USA.

Samples Characterization

FTIR (Fourier transformation infrared spectroscopy) was used to examine the functional groups of the prepared materials using a Tensor 27, Bruker, Germany. Around 5 mg of the powder was homogenized with about 100 mg of KBr with an agate mortar and was pelletized before the measurement. The surface morphology characteristics of the montmorillonite particles were

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observed by FESEM.

Adsorption Experiments

A stock Zn^{2+} solution (1000 mg L^{-1}) was prepared by dissolving $ZnCl_2$ into deionized water and diluting to prepare all synthetic fresh solutions used in the investigation. To find the optimum Zn^{2+} adsorption conditions and to study the adsorption in batch conditions, a 100 mL stoppered conical flask and a temperature-controlled shaker were used for the experiment. Dosage effects were studied in the range of 2–10 mg (initial concentration (C_o) of 20 mg L^{-1}, natural pH, 25 ºC, contact time of 1 h). The effect of contact time was studied in the time range of 1-60 min (20 mg L^{-1}, 10 mg, natural pH, 25 ºC). Adsorption equilibrium studies in a single system were carried out with initial concentrations ranging from 10 to 70 mg L^{-1}. Zn^{2+}concentrations were determined by GBC-932 atomic adsorption spectrophotometer (AAS, GBC, Australia). The adsorption capacity q_e (mg g^{-1}) which is the adsorbed amount of adsorbate per unit mass of the adsorbent at time t was calculated according to Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where, C_o and C_e (mg L^{-1}) are the initial and equilibrium Zn^{2+} concentrations, respectively. V (L) is the volume of adsorption solution and m (g) is the mass of adsorbent.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The FTIR spectrum of the sample is shown in Fig. 1a. The band observed near 1580 cm^{-1} in both samples indicates presence of a cylinder-like carbon structure (rolled graphene sheet). The morphological characteristics of the MWCNTs were investigated by SEM and are shown in Fig. 1b.

Adsorption Studies

Effect of Dosage: Presence of satisfactory adsorbent amount is an important parameter to consider as it determines the number of free adsorption sites for a given initial concentration.

The experiments were carried out at 25 ºC (the MWCNTs dosage in the range of 2–10 mg, Zn^{2+} solution volume and concentration were 25 mL 20 mg·L^{-1}, respectively). Adsorption of ions increased rapidly with the increasing dosage of adsorbent, which due to the increase in the number of active sites with increased amount of MWCNTs, as shown in Fig. 2.

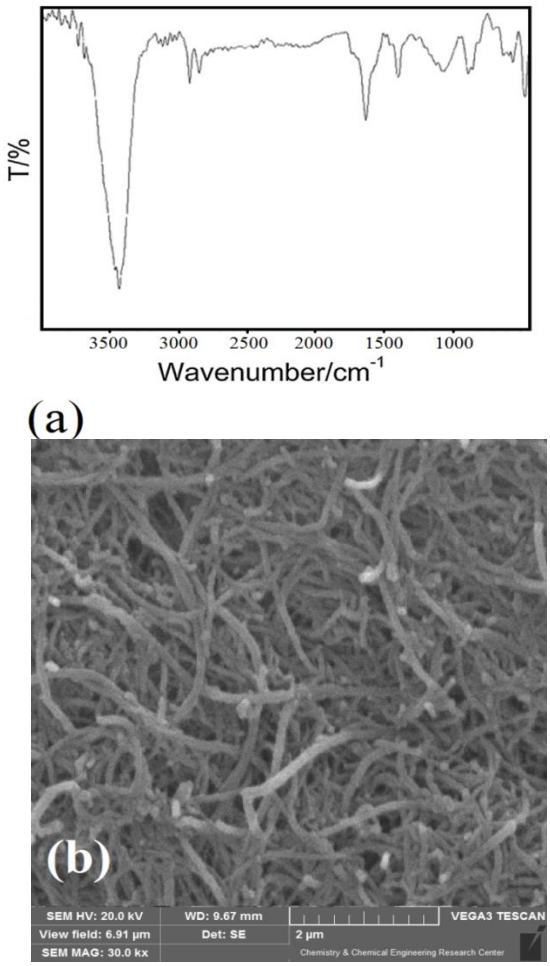

Fig. 1. FTIR spectrum (a) and SEM micrograph (b).

At 8 mg, the adsorption of Zn^{2+} reached equilibrium state. Considering the adsorption and practicality, 8 mg was selected as the optimum adsorbent dosage in the following experiments.

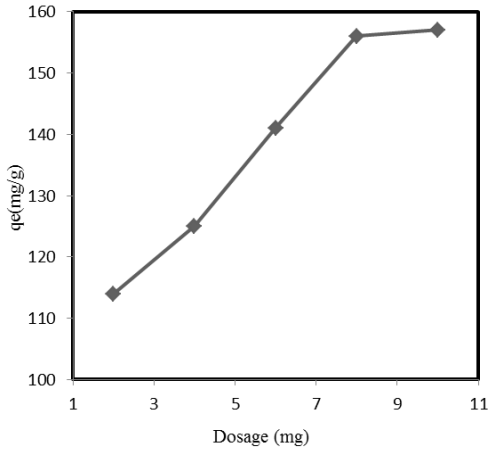

Fig. 2. Effect of adsorbent dosage (20 mg L^{-1}, natural pH, 25 ºC, 2 h).

Effect of Contact Time: One of the meaningful parameters in the design of economical wastewater treatment systems is the equilibrium time [28, 29].

The effect of contact time on the adsorption process was studied and evaluated. The investigation was executed with 8 mg of MWCNTs at natural pH and 25 ºC.

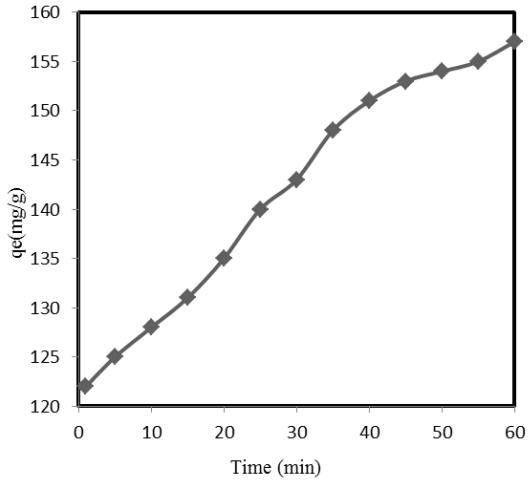

Fig. 3. Effect of contact time (20 mg L^{-1}, 10 mg, natural pH, 25 ºC).

From the results shown in Fig. 3 it is clear that the MWCNTs adsorbent exhibits a gradual increase in Zn^{2+} adsorption capacity with the increase in the reaction contact time. The metal adsorption capacity value was found to reach saturation after 55 min with maximum adsorption of Zn^{2+}. These findings refer to the binding processes of $Zn^{2+}$to the surface of MWCNTs adsorbent *via* two different steps [30]. The first is related to a linear and constant increase in the metal capacity while increasing the contact time from 1 to 55 min due to the possible occupation of the surface functional groups of the adsorbent by the target metal ion. The second step is directly related to the equilibrium and saturation conditions which require more than 55 min. Finally, this period was taken as the optimal contact time for the rest testing.

Adsorption Kinetics and Modeling: To study the kinetic mechanism that refers *to* the adsorption process, the data described in the "effect of contact time and effect of temperature" sections were used for further analysis. Different kinetic models *were* applied such as pseudo–first order, pseudo–second order and intraparticle diffusion to interpret the experimental data [31-35].

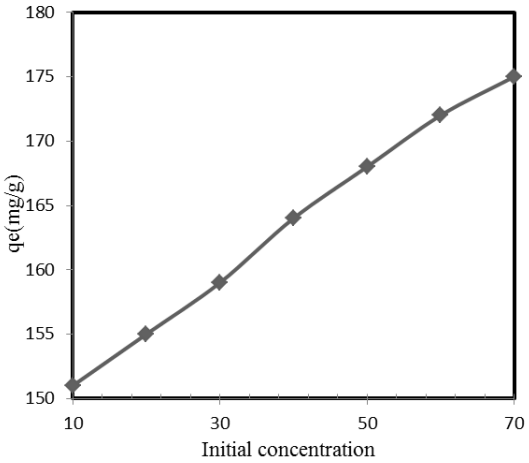

Fig. 4. Effect of initial concentration (10 mg, pH 2, 25 ºC, 60 min).

Table 1. Kinetic parameters of Zn^{2+} adsorption by MWCNTs

Model	Parameters	R^2
Pseudo–first order	q_e = 118.71 mg g^{-1} K_1 = 0.190 min^{-1}	$R_1^2 = 0.889$
Pseudo–second order	q_e = 92.9 mg g^{-1} K_2 = 0.035 g mg^{-1} min^{-1}	$R_2^2 = 0.999$
Intraparticle diffusion	k_p = 78.25 mg g^{-1} $min^{-1/2}$ C = 5.0856	$R_3^2 = 0.788$

A linear form of the pseudo–first order model could be given as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \qquad (2)$$

where, q_e and q_t are the amounts of ion adsorbed (mg g^{-1}) at equilibrium and time t, respectively. k_1 is the equilibrium rate constant (min^{-1}). The linear fit between the $\ln(q_e - q_t)$ and contact time (t) can show an approximation of pseudo–first order kinetics.

The linear form of the pseudo–second order model [33] can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + (\frac{1}{q_e})t \qquad (3)$$

where, k_2 is pseudo–second order equilibrium rate constant (g mg^{-1} min^{-1}). The linear fit between the t/q_t and contact time (t) can show an approximation of pseudo–second order kinetics.

The intraparticle diffusion model was used to explore the possibility of intraparticle diffusion resistance affecting adsorption [36]:

$$q_t = k_p t^{1/2} + c \quad (4)$$

where, k_p is the intraparticle diffusion rate constant and c is the intercept which is related to the thickness of the boundary layer. According to this model, when intraparticle diffusion is involved in the adsorption process the plot should be linear and intraparticle diffusion is the rate controlling step if the line passes through the origin [37]. All kinetic parameters obtained from the experimental data fitting using the above mentioned equations are shown in Table 1. To best describe the adsorption process, it is noticeable from Table 1 that the very high value of correlation coefficients (> 0.999), and the good fit proves that the pseudo–second order model with good correlation is the best description. This suggests that the rate–limiting step of Zn^{2+} ion onto MWCNTs is chemisorption, where valency forces are involved *via* electrons sharing or exchange between the MWCNTs and the Zn^{2+} ions [38].

Adsorption Isotherms

In order to describe the interactive behavior of adsorbate and adsorbent, adsorption isotherms were used. To estimate the adsorption capacity (Q_o), the equilibrium data were fitted using Langmuir and Freundlich models [35, 36]. Below, we can see the mathematical description of these models, Eqs. ((5) and (6), respectively):

$$\frac{1}{Q_e} = \frac{1}{Q_o} + \left(\frac{1}{Q_o K_L}\right)\frac{1}{C_e} \quad (5)$$

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (6)$$

where, Q_e is the solid phase adsorbate equilibrium amount (mg g^{-1}); Q_o is the maximum adsorption capacity (following Langmuir monolayer adsorption technique) (mg g^{-1}); K_L is Langmuir constant (L mg^{-1}); *n* and K_F (mg g^{-1})(L mg^{-1}) are Freundlich constants which are related to the adsorption intensity and adsorption capacity, respectively. The values of *1/n* and K_F are found from the slope and intercept, respectively, of the linear plot of experimental data of $\ln Q_e$ *versus* $\ln C_e$. 1/n values show the different kinds of isotherm: not reversible (1/n = 0), favorable (0 < 1/n < 1) and unfavorable (1/n > 1) [38]. Langmuir isotherm numbers of K_L and Q_o can be obtained from the intercept and slope of the linear plot of $1/Q_e$ *vs.* $1/C_e$. Table 2 shows the adsorption isotherm for Zn^{2+} ion on MWCNTs surface.

From Table 2 one can see that Langmuir isotherm demonstrates a better fit of experimental data than Freundlich isotherm. Also, this proves that the surfaces of adsorbents are primarily built of heterogeneous adsorption patches [36] and lesser homogeneous patches [39]. which is The Freundlich constant n is a measure of adsorption intensity. From Table 2 it can be seen that the values of 1/n (adsorbent) were lower than 1, which shows high adsorption intensity [40]. Results show that MWCNTs surface is better in adsorption of Zn^{2+} ion. R_L, a dimensionless parameter is used to show the favorability of adsorption process of Zn^{2+} ion onto adsorbent surfaces. The mathematical definition of R_L is as follows:

$$R_L = \frac{1}{1+K_L C_O} \quad (7)$$

In terms of R_L, the adsorption process can be seen as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) [41-43]. From the results it was noticeable that in case of MWCNTs surface, the value of R_L for adsorption of Zn^{2+} ion was between 0 and 1. So, the adsorption of Zn^{2+} onto the adsorbent is favorable. MWCNTs has an adsorption capacity of about 93 mg g^{-1}.

Table 2. Fitting experimental data of Zn^{2+} adsorption to the equations of Langmuir and Freundlich.

Model	Parameters	R^2
Langmuir	$Q_o = 93$	0.999
	$K_L = 4.98$	
Freundlich	1/n = 0.611	0.998
	$K_F = 54.8$	

CONCLUSIONS

Multi-walled carbon nanotubes (MWCNTs) are an effective adsorbent for the removal of Zn^{2+} from aqueous solutions. Adsorption capacity depends on adsorbent dosage, contact time and initial metal ion concentration. Langmuir and Freundlich isotherms were used to determine the adsorption parameters and the data of equilibrium are best described by Langmuir model which gives the value of 93 mg g^{-1} as the maximum adsorption capacity. The adsorption process was studied kinetically and the obtained data were analyzed using the pseudo–first order, pseudo–second order, intraparticle diffusion models. Pseudo–second order was found to be the best correlation model based on the values of the correlation coefficient (R^2). Therefore, it can be concluded that the MWCNTs have potentiality and are a promising adsorbent for environmental management and water treatment due to their better efficiency and feasibility.

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КИНЕТИЧНО ИЗСЛЕДВАНЕ И МОДЕЛИРАНЕ НА ОТСТРАНЯВАНЕТО НА Zn^{2+} ОТ ОТПАДНА ВОДА ЧРЕЗ АДСОРБЦИЯ ВЪРХУ МНОГОСТЕННИ ВЪГЛЕРОДНИ НАНОТРЪБИЧКИ

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(Резюме)

Представени са адсорбционни методи за отстраняване на токсичния метален йон Zn^{2+} с адсорбент многостенни въглеродни нанотръбички (MWCNTs). SEM и FTIR методи са използвани за охарактеризиране на MWCNTs. Изучена е връзката между оптимизационните фактори (количество адсорбент, време на контакт и начална концентрация ва токсичния метален йон) и адсорбционните свойства на MWCNTs. Количеството метал, адсорбирано за различни интервали от време, е в основата на адсорбционната кинетика. Моделирани са кинетичните криви. Установено е, че адсорбцията на Zn^{2+} съответства на модел от псевдопърви порядък ($R^2 > 0.999$) и времето за достигане на адсорбционно равновесие е 55 min. Равновесните адсорбционни данни съответстват на изотермния модел на Langmuir.