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ADSORPTION OF CADMIUM IONS ISOTHERM FROM WATER INTO POLYMER NANOCOMPOSITE

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Polymer nanocomposite with zerovalent iron particles was used to remove Cd^{2+} from water. The adsorption of Cd^{2+} was examined as a function of initial metal ion concentration. Also, the equilibrium data were analyzed on the basis of various adsorption isotherm models, specifically Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich. The results showed that the adsorption process was in agreement with the Langmuir isotherm model.

Keywords: *polymer nanocomposite***,** *adsorption, Langmuir isotherm***,** *cadmium ions*

INTRODUCTION

Cadmium is a toxic heavy metal of particular environmental and occupational importance [1]. It is discharged into the environment through the combustion of fossil fuels, metal production, application of phosphate fertilizers, electroplating, and the manufacturing of batteries, pigments, and screens [2–4]. This heavy metal leads to serious contamination of both soil and water. Cadmium has been classified as a human carcinogen and teratogen affecting lungs, kidneys, liver and reproductive organs [1,5]. The World Health Organization (WHO) has set a criterion of maximum concentration of 0.003 mg/L for Cd in drinking water [6]. Given the pervasive cadmium contamination and the low drinking water basis, there is an upsurge of interest in the development of techniques to remove cadmium from contaminated water. Thus, scholars are focusing on the removal and recovery of cadmium, including various methods such as chemical precipitation [7], reduction–oxidation [8], ion-exchange [9], forward osmosis [10], biological process [11] which have been introduced for removal of cadmium from the aqueous solution. Among the different methods described above, adsorption process is attractive in consideration of its efficiency, economy and ease of operation, especially as lots of studies on the theme have been carried out [12–14].

The objective of the research is to inquire into the adsorption isotherm models and the cadmium removal by polymer nanocomposite (PNC).

MATERIALS AND METHODS

Preparation of PNC

For preparation of PNC, commercial, sulfonated styrene–divinylbenzene and cross-linked copolymer has been used as polymer. Note that the synthesis of PNC is based on borohydride reduction of Fe^{2+}. Polymer (1.0 g) has been added to the stirred ethanol solution of $FeCl_2{\cdot}4H_2O$ (0.4 M, 300 ml). Also, 1M $NaBH_4$ solution has then been added drop-wise to the Fe-polymer mixture with continuous stirring of the resulting solution. After the addition of $NaBH_4$ solution, the mixture has been stirred for additional 20 min, PNC collected and washed thrice with iso-propanol to prevent oxidation. Deionized deoxygenated water (sparged with nitrogen) used to prepare aqueous solutions.

Adsorption studies

Batch adsorption experiments have been carried out to enable an accurately weighted amount of PNC reach equilibrium with Cd^{2+} aqueous solutions of various initial concentrations between 20 and 400 mg/L and temperatures ranging around 25 °C. Besides, the weighed samples of sorbent (0.1 g) have been placed into bottles and filled up with solutions (0.3 L). The bottles underwent stirring by a temperature-controlled shaker (IKA, Germany). In 24 hours the solution has been filtrated and the concentration of Cd^{2+} in filtrate determined. The adsorption capacity (*q*, mg/g) and adsorption degree (*R*, %) has been calculated by the following equations:

$$q = \left(C_0 - C_{eq}\right)\cdot\frac{V}{m} \quad (1)$$

$$R = \frac{\left(C_0 - C_{eq}\right)}{C_0}\cdot 100\% \quad (2)$$

where C_0, C_{eq} – initial and equilibrium concentration of Cd^{2+} in solution respectively, mg/L, *V* – solution volume and *m* – sorbent dose (g).

All experiments have been performed in duplicate.

RESULTS AND DISCUSSION

Effect of initial Cd^{2+}concentration on adsorption process.

Table 1 shows that the equilibrium adsorption capacity of sorbent rises together with the increase of initial concentration of Cd^{2+} up to 420 mg/L. This is explained as being due to the fact that the initial concentration of solute provides the major driving force to overcome the mass transfer resistance. Rise in loading capacity of PNC at high initial concentrations of Cd^{2+} may also be due to the appreciable interaction between metal ions and sorbent surface.

Table 1. Equilibrium uptake capacities and adsorption degree at different initial concentrations for Cd^{2+}

C_0, mg/L	q_{eq}, mg/g	R, %
20	5.9	89.00
40	11.5	86.00
60	16.4	82.17
80	21.5	80.75
100	26.2	78.60
125	31.4	75.36
150	37.1	74.20
175	43.0	73.66
200	47.8	71.70
225	52.8	70.36
250	56.5	67.76
275	60.3	65.75
300	62.4	62.43
325	64.2	59.26
350	67.0	57.40
380	67.7	53.47
400	69.2	51.90
420	69.8	49.88

The maximum value of adsorption degree was identified as being due to 89.00 % at 20.0 mg/L. The results demonstrate a tendency toward decrease in adsorption degree as the initial Cd^{2+} concentration rose. At low initial concentrations all sorbate from the adsorption medium tend to interact with binding sites of the sorbent leading to higher degrees of adsorption. In contrast, at high initial concentrations of Cd^{2+}, low adsorption degrees became apparent due to the saturation of adsorption sites.

Adsorption isotherms

Equilibrium data may be analyzed using well-known adsorption isotherms which provide for the basis of adsorption systems. The most widely used isotherm equation for modeling the adsorption data is the Langmuir equation which is valid for monolayer sorption on the surface with a finite number of identical sites defined by Equation (3).

$$q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \quad (3)$$

where K_L is the adsorption equilibrium constant representing the affinity of binding sites (L/g) and q_{max} is the maximum amount of AR per PNC unit weight to form a complete monolayer on the surface (mg/g). It presents a practical limiting adsorption capacity in case where the surface is fully covered with metal ions. q_{max} and K can be determined from the linear plot of C_{eq}/q_{eq} versus C_{eq} [15].

The Freundlich model is an empirical equation based on sorption on the heterogeneous surface. It is given as:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (4)$$

where K_F and n are the Freundlich constants that indicate relative capacity and adsorption intensity, respectively. The Freundlich equation can be linearized by taking logarithms and constants [16].

Temkin isotherm is another adsorption model considering adsorbent–adsorbate interactions. The model assumes that these interactions cause a decrease in the heat of adsorption of molecules in the layer and the binding energies show a uniform distribution in the adsorption process [17]. This isotherm can be expressed by the following formula:

$$q_e = B \ln A + B \ln C_{eq} \quad (5)$$

In Equation (5) constant A denotes Temkin constant used to examine adsorbate–adsorbate interactions and B is the constant related to adsorption heat. A and B can be determined from plot of q_e vs. lnC_e.

The Dubinin–Radushkevich isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character, involves van der Waals forces and is applicable for physical adsorption processes. The Dubinin-Radushkevich [18] equation has the following form

$$q_e = q_m e^{-\beta\varepsilon^2} \quad (6)$$

where q_m is the theoretical isotherm saturation capacity (mg/g), β is a constant related to the sorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows

$$\varepsilon = RT \ln(1 + \tfrac{1}{C_{eq}}) \quad (7)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature.

The constant β gives the mean free energy, E, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship

$$E = \frac{1}{\sqrt{2\beta}} \quad (8)$$

The β, and q_m parameters can be determined from plot of lnC_{eq} versus ε^2.

All obtained isotherm constants and correlation coefficients are listed in Table 2.

Table 2. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm model parameters and correlation coefficients for adsorption of cadmium on PNC

Langmuir	Parameters		
	K_L, L/g	q_{max}, mg/g	r^2
	0.022	90.91	0.9940
Freundlich	Parameters		
	K_F	n	r^2
	4.677	1.842	0.9740
Temkin	Parameters		

	A	B	r^2	
	0.3878	16.47	0.9570	
Dubinin-Radushkevich	Parameters			
	$q_{m,}$	$\beta\,10^6$,	E, kC/mol	r^2
	44.36	2.0	0.5	0.5570

As the four systems reviewed, Langmuir isotherm correlates (r^2 > 0.9900) rather with the experimental data of adsorption equilibrium of Cd^{2+} on the PNC than Freundlich, Temkin and Dubinin-Radushkevich isotherms. The adsorption data of metal ions in accordance with the Langmuir isotherm shows that the binding energy of the entire surface of PNC is uniform. By the way, the whole surface has an identical adsorption activity. In line with Langmuir isotherm, the adsorption data of Cd^{2+} also show that the adsorbed ions do not interact or compete with each other to form a monolayer. This phenomenon also indicates that chemisorption has the principal removal mechanism in the adsorption process. The maximum adsorption (q_{max}) values for Cd^{2+} are in good accordance with the experimentally obtained values.

As seen from Table 2, according to Freindlich model the *n* value was found to make up above >1.0. The value of *E* as set forth in Dubinin-Radushkevich model is less than 1 kC/mol. From this it follows that the physical adsorption process prevails. However, in line with this model the value of correlation coefficient the regression parameter r^2 (0.5570) showed that this isotherm model did not provided a very good fit to the experimental data.

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ИЗОТЕРМА СОРБЦИИ ИОНОВ КАДМИЯ ИЗ ВОДЫ НА ПОЛИМЕРНОМ НАНОКОМПОЗИТЕ

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Для удаления ионов Cd^{2+} из воды использовали полимерный нанокомпозит с нульвалентными частицами железа. Адсорбцию Cd^{2+} исследовали в зависимости от начальной концентрации иона металла. Данные о равновесии анализировали на основе различных моделей изотерм адсорбции, а именно, Ленгмюра, Фрейндлиха, Темкина и Дубинина-Радушкевича. Результаты показали, что процесс адсорбции согласуется с моделью Ленгмюра.
Ключевые слова: *полимерный нанокомпозит, адсорбция, изотерма Ленгмюра, ионы Cd^{2+}*

KADMİUM İONLARININ SULU MƏHLULLARDAN POLİMER NANOKOMPOZİTLƏ SORBSİYA İZOTERMİ

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Kadmium ionlarının sudan kənarlaşdırılması üçün tərkibində sıfır valentli dəmir hissəcikləri olan polimer nanokompozit istifadə olunmuşdur. Kadmium ionlarının sorbsiyası metal ionlarının ilkin qatılığından asılı olaraq tədqiq edilmişdir. Sorbsiya izotermi Lenqmür, Freyndlix, Temkin və Dubinin-Raduşkeviç modellərilə işlənmişdir. Müəyyən olunmuşdur ki, sorbsiya prosesi Lenqmür izoterm modeli ilə yaxşı təsvir olunur.
Açar sözlər: *polimer nanokompozit, adsorbsiya, Lenqmür izotermi, kadmium ionları*

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