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Zinc Adsorption Properties of Alginate-SBA-15 Nanocomposite

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P A P E R I N F O

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Assessment of adsorption zinc (II) ions from aqueous solution using alginate-SBA-15 sorbent nanocomposite was investigated as a function of zinc concentration, solution pH, and contact time. For that purpose, the alginate-SBA-15 nanocomposite adsorbent was prepared through encapsulation method by immobilization mesoporous SBA-15 into a polymeric matrix. Identification of functional groups and surface morphology of the obtained nanocomposite was carried out by X-Ray diffraction (XRD), scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FTIR) and nitrogen porosimetry experiments. Sorption performance of the alginate-SBA-15 adsorbent during batch experiments was studied. A mathematically explanation of adsorption process using kinetics and isotherm models was also performed. Kinetic study was revealed that the pseudo second-order model has good agreement with the experimental results than the pseudo first-order model. Therefore, it indicates that the concentration of both alginate-SBA-15 and zinc metal ions are involved in the rate determining step of the sorption process. The q_{max} value for zinc (II) ions adsorption onto alginate-SBA-15 was found 46.3 mg g^{-1}. According to thermodynamic analysis, physisorption and the endothermic of the sorption process nature of Zn(II) ions onto alginate-SBA-15 nanocomposite was revealed.

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1. INTRODUCTION

The world pollution phenomena can regularly attributed to the rapid industrialization and large consumption of harmful materials, especially heavy metals. Various hazardous effects of heavy metals well recognized on different kinds of environmental ecosystems. Heavy metal ions can be strongly dangerous to biosystems because they are non-biodegradable and can gather up in sediments, soil and water. For example, zinc, the main source of alloying industries which its world consumption of metal usage in 2014 was recorded 13521 thousand metric tons, is produced by pyrometallurgical and hydrometallurgical processes from its minerals [1, 2, 4]. Production of such large amount of zinc metal requires huge treatment of ore rocks, means that a lots quantity of liquid effluents will generates. The propagating of the exhausted wastes into aquifers and in surface run-offs and so entering into the food chain through potable water and irrigation could cause severe injuries on living organisms. Toxicity effects of overt zinc exposure to the human body are well known so that its symptoms include loss of appetite, dyspnea, nausea, vomiting, epigastric pain, lethargy, and fatigue [5]. According to the WHO, maximum allowable limit for zinc in the drinking water is recommended as 5.0 $mg.L^{-1}$ [6]. Thus, safe disposal of the zinc wastes into environment using certified processes must be ensured.

As for removal of zinc from wastes, so far several different physical and chemical processes have been trialed. Precipitation [7], membrane filtration [8], ion exchange [9], and adsorption [10, 11] are just few instances. However, the later technique has more significant features for the removal of zinc than the others. Low cost, easy operation, maximum sorption capacity and regeneration ability of the adsorption process convert it as an efficient process for the heavy metals removal. Various sorbents such as clinoptilolite [6], modified activated carbon [12], natural bentonite

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[13], bagasse fly Ash [14], natural clay [15] and azolla filiculoides [16] can be also used in the removal of zinc from both industrial and municipal wastewaters.

Alginate is a polysaccharide biopolymer which has lot of carboxyl and oxygen-containing functional groups on its surface. Additionally, great numbers of chains in its polymeric matrix structure form electronegative cavities enable it as a proper adsorbent for trapping cations via ionic interaction. So, aforementioned features of the alginate can lead to cross-linking and substitution of metal ions with those cavities and functional groups. Choi et al. through the zinc adsorption by functionalized alginate shows that it has high adsorption capacity and is able to remove several pollutants, simultaneously [17].

On the other hand, great deals of researches on the harmful material adsorption as well as heavy metal removal using nanoporous adsorbent have been performed [18-22]. Since the nonoporous adsorbents have large surface area and pore size, the attention toward using these materials was considerably intensified. For instance, a work reported Zn^{2+} adsorption using the modified MCM-41 with 5-mercapto-1-methyltetrazole [23]. By 2009, Pérez-Quintanilla et al. have synthesized a hybrid SBA-15-based material sorbent and have used in zinc removal from water [24]. Nonetheless, there is no report on zinc removal using alginate-SBA-15 by adsorption.

The ultrafine structure of nanoporous adsorbents such as SBA-15 caused some difficulties, such as difficult filtration in the separation process. For solving this problem, the authors demonstrated a technique, based on encapsulation of SBA-15 by alginate as a suitable biopolymer supporter.

Hence, the present study is aimed at synthesizing alginate-SBA-15 nanocomposite, based on immobilization SBA-15 into the matrix of alginate by encapsulation technique. The first part of this work is devoted to synthesis and characterization of alginate-SBA-15 and the last part is allocated to investigation of the adsorption ability of the obtained nanocomposite on the removal of zinc (II) ions from aqueous solution.

2. EXPERIMENTAL

2. 1. Materials Stock solutions of zinc ions (1000 ppm) were prepared by dissolving 2.06 g zinc nitrate tetrahydrate, $Zn(NO_3)_2.4H_2O$,in 500 ml distilled water. Pluronic P123 triblock copolymer (EO_{20}-PO_{70}-EO_{20}) and sodium alginate were obtained from Sigma-Aldrich (Milwaukee, WI, USA). All other minor material and solvents used were of analytical grade from Merck (Darmstadt, Germany).

2. 2. Instruments A Philips X'pert powder diffractometer system with Cu-Kα (λ=1.541 Å) radiation from 1.5° to 10° (2θ) at a scan rate of 0.02° (2θ) s^{-1} was utilized for X-ray analysis. A Bruker FTIR spectrophotometer of model Vector-22 over the wave number range of 4000-400 cm^{-1} was used. Nitrogen adsorption-desorption analysis were performed using a Quantachrome NOVA 2200e at 77 K. A LEO 1455VP scanning electron microscopy was also utilized for morphological identification. Determination of the zinc content of samples was conducted using an inductively coupled plasma-optical emission spectroscope (ICP-OES) Varian turbo model 150-Axial Liberty.

2. 3. Alginate-SBA-15 Preparation Nanocomposite alginate-SBA-15 was prepared via a three-step method. First, nanoporous silica SBA-15 was produced according to our previous work [25]. Given amounts of 2 M HCl solution as acidifier and 4 g pluronic P123 triblock copolymer surfactant (EO_{20}-PO_{70}-EO_{20}) as template were introduced to a beaker, after that, the silica precursor (etraethylorthosilicate) was added. The resulting mixture was just situated under stirrer and aging condition for 8 and 24 h, subsequently. Then, it was washed and rinsed, and at the second step, calcination was performed at 550 °C for 6 h for elimination of residual organic species (i.e. triblock copolymer). At third-step, suspension of SBA-15 was prepared by adding 1.5 g of SBA-15 powder in 10 mL pure water. After 30 min sonication, it was added to a solution containing 100 mL of the 1.5% sodium alginate solution and was dispersed in high speed for 2 h. After that, it was added into 0.1 mol L^{-1} $Ca(NO_3)_2$ solution through a 0.3 mm medical needle. Gel type spherical beads were formed during this process. For hardening the formed composites, it was gently stirred in the above mentioned solution for 3 h. The prepared composites washed three times with pure water and, finally, dried at 40 °C for about 10 h. According to the weight ratios of sodium alginate and SBA-15 before the mixing stage, the amount of SBA-15 was 50% in composite. The granules of calcium alginate were prepared in a similar way with dropwise addition of sodium alginate into $Ca(NO_3)_2$ solution.

2. 4. Batch Adsorption Experiments Assessment of zinc (II) ion removal using alginate-SBA-15 nanocomposite was investigated by batch equilibrium experiments. 10 mg of prepared adsorbent for each experiment was added to 10 ml of zinc solution of given concentration. The pH value was adjusted by 0.1 M NaOH and HCl solution. The mixture was shaken for a desired time using a water bath shaker of model CH-4311 (Infors AG). After reaching equilibrium, the solution was then separated from adsorbent using filtration and was analyzed with ICP-OES, for its zinc content. The adsorption capacity (q, mg g^{-1}) was calculated using following relationship (Equation(1)):

Adsorption capacity :

$$q(mg\ g^{-1}) = (C_i - C_f) * \frac{V}{m} \quad (1)$$

where, C_i and C_f are initial and final concentration of zinc ions (mg L^{-1}), V is the volume of zinc solution (ml), m is the mass of adsorbent (g), and q is the adsorption capacity of the sorbent (mg g^{-1}).

2. 5. Adsorption Isotherms To reveal the relationship between the quantity of zinc ions adsorbed on the alginate-SBA-15 surface and the concentration of remaining zinc ions in the aqueous phase, the adsorption isotherm studies were carried out. As for isotherm description of adsorption process so far several binding models have been introduced [26, 27]. The Langmuir and Freundlich isotherm models were selected in this case. The isotherms are mathematically expressed as follows (Equation(2) and (3)):
Langmuir isotherm [28]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} k_l} + \frac{C_e}{q_{max}} \quad (2)$$

Freundlich isotherm [28]:

$$\log q_e = \log k_f + \frac{1}{n} C_e \quad (3)$$

where, q_e (mg g^{-1}) and q_{max} (mg g^{-1}) represent the amount of zinc ions adsorbed per unit weight of the adsorbent and the maximum sorption capacity, respectively. C_e (mM L^{-1}) is the equilibrium concentration of the zinc (II) in solution, and k_l (L mM^{-1}) is Langmuir isotherm constant which relates to the energy of adsorption. k_f is the measure of adsorption capacity and n is the adsorption intensity, which both of them are the Freundlich constants.

2. 6. Adsorption Kinetics For describtion of the mechanism of sorption process, the kinetics studies were performed. Out of several mathematical models, the pseudo first-order and pseudo second-order models were selected to assessment of adsorption process. The kinetics models are described by following equations (Equation(4) and (5)):
Pseudo first-order model [29]:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \left(\frac{K_1}{2.303}\right) t \quad (4)$$

Pseudo second-order model [29]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where, q_e and q_t stand for the quantity of zinc adsorbed (mg g^{-1}) onto adsorbent at equilibrium and at time t, respectively, and K_1 (L min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the rate constant of adsorption. The straight line graph of $\log(q_e - q_t)$ versus t and (t/q_t) versus t for different initial concentrations of the zinc (II) ion were used to calculate the quantity of K_1 and K_2, respectively.

2. 7. Thermodynamic Study Evaluation of the temperature effect on thermodynamic criteria was investigated. Following equations (Equations (6), (7) and (8) were applied on the equilibrium experimental result:

$$K_d = \frac{(C_i - C_f)}{C_f} \frac{V}{m} \quad (6)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

where, K_d (L g^{-1}) is the distribution coefficient. T (K) is the temperature and R (8.314 J mol^{-1} k^{-1}) is the universal gas constant. ΔG°, ΔH° (KJ mol^{-1}) and ΔS° (J K^{-1} mol^{-1}) are standard free energy change, standard enthalpy change and standard entropy change, respectively.

3. RESULT AND DISCUSSION

3. 1. Characterization The XRD patterns of alginate-SBA-15 nanocomposite is given in Figure 1a. The alginate-SBA-15 represents an intense peak at 2θ smaller than 3°, accompanying some small peaks. Under such case, formation of mesoporous SBA-15 and the presence of SBA-15 in the alginate-SBA-15 can be confirmed [25].

The IR spectrum of the alginate-SBA-15 was illustrated in Figure 1b. Adsorption bands at 3450, 2900, 1610, 1429, 1125, and 1065 cm^{-1} are relate to hydroxyl (-OH), carbon-hydrogen (-CH), carboxyl (-COOH), carboxyl (-COOH), carbon-oxygen bond of ether group, and carbon-oxygen bond of alcohol group, respectively [30, 31].

The nitrogen adsorption/desorption isotherms of the alginate-SBA-15 nanocomposite shown in Figure 1c represents a sorption profile of type IV means that an assemblage of non-intersecting tubular pores was occurred. Such condition is generally associated with mesoporous adsorbents [32]. The sorption profile consisted of a step condensation behavior due to the formation of mesoporous in the SBA-15 and the presence of mesoporous SBA-15 in the alginate-SBA-15 [3, 33-35].

Pore volume, specific surface area, and pore diameter of the samples are tabulated in Table 1. Among the samples, the surface area of SBA-15 so far is higher than the others. Similar behavior can be observed in all three properties of SBA-15 rather than alginate-SBA-15. This condensation effect may be due to the polymerization of monomers inside the channels of SBA-15 as a result of encapsulation method.

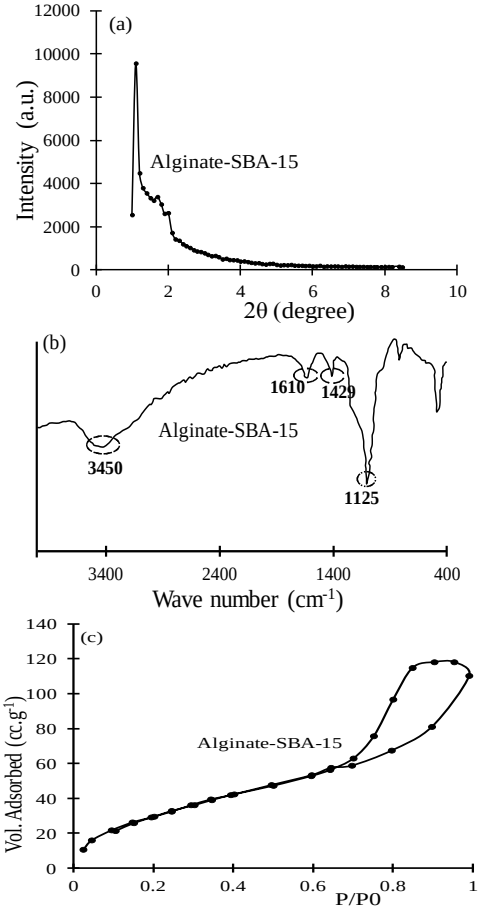

Figure 1. (a) XRD patterns; (b) FTIR spectra; (c) Nitrogen adsorption/desorption isotherms of alginate-SBA-15

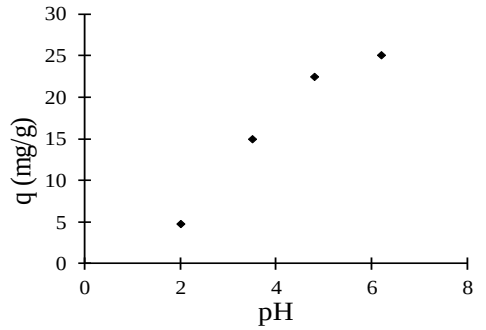

Figure 2. Effect of pH on zinc ions adsorption using the alginate-SBA-15 nanocomposite

TABLE 1. Morphological properties of Ca-alginate, SBA-15 and alginate-SBA-15

Sample	Pore volume ($cm^3 g^{-1}$)	Surface area ($m^2 g^{-1}$)	Pore diameter (nm)
Ca-alginate	0.009	3.8	2.29
SBA-15	0.74	749	12.6
Alginate-SBA-15	0.17	122	9.7

SEM images of the nanoporous SBA-15 and alginate-SBA-15 nanocomposite were presented in our previuos work [25]. The image of SBA-15 illustrates a wavy surface with some ripples together with lateral dimensions. Regarding to the SEM images, the average size of the SBA-15 is 0.2 µm and the dimension of the alginate-SBA-15 is 650 µm. Also image of alginate-SBA-15 nanocomposite show that the SBA-15 regularly distributed alongside the microcapsules surface, resulting in the adsorbent specific surface area was incremented.

3. 2. Effect of pH The effect of working solution pH ranging from 2.0 to 6.2 on the sorption ability of alginate-SBA-15 nanocomposite for Zn (II) adsorption was investigated and represented in Figure 2. The adsorption behavior of alginate-SBA-15 on removal of zinc ions from aqueous solution was significantly affected by the pH. The synergic effect of functional groups in both SBA-15 and alginate takes part in this phenomenon. Hereupon, sorption situations of zinc are improved with deprotonation of carboxyl groups in alginate; on one hand, and the hydroxyl groups existing in both SBA-15 and alginate have a proton exchange abilities with zinc ions at the higher pHs; on the other hand. Such conditions can be represented as the following reactions [25]:

Acidic region:

$$HOOC–Alginate–OH+H^+ \rightleftharpoons HOOC–Alginate^+ + H_2O \quad (1)$$

$$SBA–OH + H^+ \rightleftharpoons SBA^+ + H_2O \quad (2)$$

Alkaline region:

$$HOOC–Alginate–OH + 2OH^- \rightleftharpoons {}^-OOC–Alginate–O^- + 2\,H_2O \quad (3)$$

$$SBA–OH + OH^- \rightleftharpoons SBA–O^- + H_2O \quad (4)$$

where, HOOC–Alginate–OH and SBA–OH denote alginate and mesoporous SBA-15 in alginate-SBA-15. Functional groups existing on surface of both alginate and SBA-15 (i.e. -COOH and -OH) can function as the binding sites for capturing Zn^{2+} ions. Zinc ions were chiefly retained by electrostatic interaction with those functional groups. Under such condition, alginate-SBA-15 behaves as an ion-exchanger with -COOH and -OH groups, which act as the functioning sites. These finally can lead to absorption of large numbers of Zn^{2+} ions by the functional groups.

3. 3. Adsorption Isotherm Figure 3a shows the variation of the extent of sorption process with concentration of zinc ions represent that by increasing in the zinc concentration of the solution, the metal uptake capacity increases. Albeit, it seemed that both Langmuir and Freundlich isotherm models are capable

of satisfactorily representing the equilibrium data (see Figures 3b & 3c), however, the former shows a better verification. Thus, it indicates that the sorption process is affected by the formation of monolayer coverage of the sorbate (zinc) on the homogenous sorbent surface. The Langmuir and Freundlich parameters are listed in Table 2.

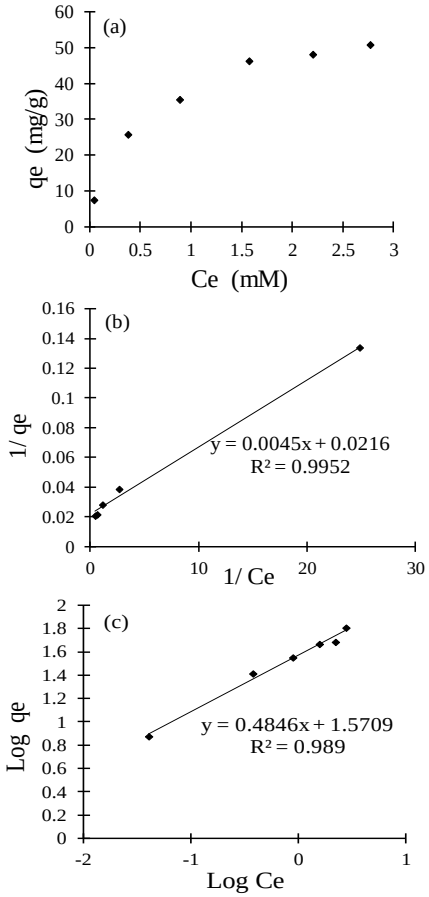

Figure 3. (a) Effect of initial concentration of zinc ions on adsorption capacity of alginate-SBA-15; (b) Langmuir adsorption isotherm curve of Zn(II) ions uptake onto alginate-SBA-15 ; (c) Freundlich adsorption isotherm curve of Zn(II) ions uptake onto alginate-SBA-15

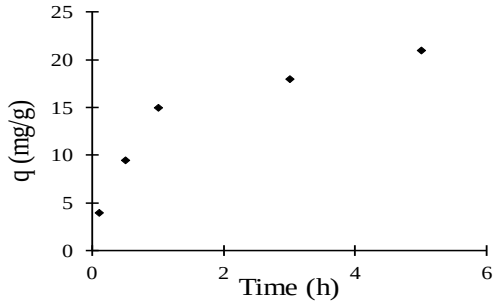

Figure 4 . Effect of contact time on Zn (II) adsorption performance of alginate-SBA-15 nanocomposite

TABLE 2. Freundlich and Langmuir isotherm parameters for adsorption of zinc ions using alginate-SBA-15

	q_{max} (mg g^{-1})	46.296
Langmuir	K_l (L $mMol^{-1}$)	4.800
	R^2	0.995
	n	0.484
Freundlich	K_f (mg g^{-1} mM^{-1})	37.230
	R^2	0.989

3. 4. Kinetic Study The adsorption capacity of zinc adsorption using alginate-SBA-15 as a function of contact time is sketched in Figure 4 ranging from 5 min to 6 h at the zinc initial concentration of 100 ppm and 10 mg of alginate-SBA-15. It can be seen that the uptake of zinc ions were rapidly increased and a contact time of 4 h is approximately enough to achieve equilibrium. It is believed that the presence of oxygen-containing functional groups on both alginate and SBA-15 as synergistic effect take parts in this process.

In order to investigate the mechanism of zinc adsorption using alginate-SBA-15 nanocomposite, kinetics studies were performed. To do so, the pseudo first-order and pseudo second-order models were applied on equilibrium sorption data.

Based on the regression correlation coefficient (R^2) and according to Figures 5a & 5b, the pseudo second-order model, it was observed that the pseudo second-order model has good agreement with the experimental results than the pseudo first-order model. Therefore, the conformity of pseudo second-order model result with experimental ones indicates that the concentration of both alginate-SBA-15 and zinc metal ions are involved in the rate determining step of the sorption process [36].

3. 5. Thermodynamic Study The effect of temperature on removal of zinc ions by alginate-SBA-15 nanocomposite was also investigated. Calculated thermodynamic constants using the Equations (6), (7) & (8) are listed in Table 4. The calculated ΔG° value (ΔG°= -6.204 kJ mol^{-1}) suggests that the sorption process of zinc on the alginate-SBA-15 could be considered as the physisorption process. It was found that ΔG° for physisorption is generally between -20 and 0 KJ mol^{-1}, the physisorption together with chemisorptions within -20 to -80 KJ mol^{-1}, and pure chemisorptions in the range of -80 to -400 KJ mol^{-1} [36]. The positive value of ΔH° shows that the sorption of zinc ions on alginate-SBA-15 is an endothermic process in nature. Furthermore, the positive value of ΔS° depicts the affinity of alginate-SBA-15 toward Zn(II) in aqueous solution.

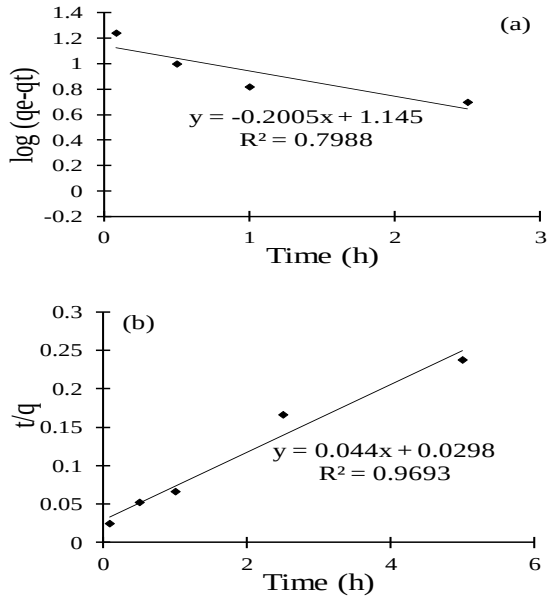

Figure 5. (a) Plot of pseudo first-order model and (b) linearized experimental data of pseudo second-order model curve

TABLE 3. Kinetics parameters

Pseudo first-order	k_1 (min^{-1})	0.4617
	q_e (mg g^{-1})	13.96
	R^2	0.7988
Pseudo second-order	k_2 (g mg^{-1} min^{-1})	0.065
	q_e (mg g^{-1})	22.72
	R^2	0.9693

TABLE 4. Thermodynamic parameters of zinc (II) ion uptake onto alginate-SBA-15

ΔG° (kJ mol^{-1}) at 25°C	**ΔH° (kJ mol^{-1})**	**ΔS° (J K^{-1} mol^{-1})**
-6.204	15.43	0.0726

TABLE 5. Quantitative comparison of zinc (II) adsorption by similar adsorbents to alginate-SBA-15 in this study with other substances from literatures.

Adsorbate	**q_{max} (mg g^{-1})**	**Ref.**
SBA-15(SH)	19	[38]
SBA-15	6.9	[37]
SA–SBA-15 [a]	26	[37]
SA–SG [a]	17	[37]
G3-PAMAM-SBA-15	12	[39]
EDTA-G3-PAMAM-SBA-15	10.4	[39]
Alginate [b]	4.3	[17]
Alginate-SBA-15	46.3	This work

[a] Functionalized with N-propylsalicylaldimine
[b] Alginate complex is impregnated with zeolite and activated carbon.

3.6. Quantitative Comparison of Alginate-SBA-15 Adsorbent Performance with Literature Data

The maximum adsorption capacity of the alginate-SBA-15 was evaluated as 46.3 mg g^{-1}, which is much higher than those of SBA-15 and functionalized alginate [17, 37]. In comparison with other substances reported in the literature [17, 37-39] given in Table 5, the sorption behavior of alginate-SBA-15 is also competitive, ranking it among the co-groups of alginate and SBA-15 synthetic sorbents as the most effective material for the Zn(II) removal.

The high adsorption efficiency of the alginate-SBA-15 is probably due to the involvement of functional groups in both alginate and SBA-15 (synergistic effect). Moreover, the alginate-SBA-15 preparing method is much easier than those of G3-PAMAM-SBA-15 and EDTA-G3-PAMAM-SBA-15. In addition, the ultrafine structure of nanoporous adsorbents such as SBA-15 caused some difficulties, such as difficult filtration in the separation process. The appropriate physical form and high mechanical stability of alginate-SBA-15 overcome these limitations.

The high adsorption efficiency of the alginate-SBA-15 nanocomposite is probably due to the synergistic effect of functional groups in both alginate and SBA-15.

4. CONCLUSION

This study was aimed for synthesizing of alginate–SBA-15 nanocomposite by encapsulation method. Through that method, the nanoporous SBA-15 was immobilized in the biopolymeric matrix of calcium alginate and was used for removing zinc (II) ions from wastewaters. According to the isotherms constants, the Langmuir isotherm showed better agreement with the experimental result than the Freundlich isotherm describing homogenous surface with identical binding sites for alginate-SBA-15. The q_{max} value for zinc (II) ions adsorption onto alginate-SBA-15 was found 46.3 mg g^{-1}.

The kinetics study of zinc removal using alginate-SBA-15 reveals that the pseudo second-order equation has close coincidence with experimental equilibrium data. The aforementioned indicates that the rate determining step of sorption process is affected by the concentration of both adsorbent (alginate-SBA-15) and sorbate (Zn). According to thermodynamic analysis, physisorption and the endothermic of the sorption process nature of Zn(II) ions onto alginate-SBA-15 was revealed. The ultrafine structure of nanoporous adsorbents such as SBA-15 caused some difficulties, such as difficult filtration in the separation process. The appropriate physical form and high mechanical stability of alginate-SBA-15 overcome these limitations.

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Zinc Adsorption Properties of Alginate-SBA-15 Nanocomposite

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چکیده

در مقاله حاضر، جذب یون روی از محلول آبی با استفاده از نانوکامپوزیت alginate-SBA-15، به عنوان تابعی از غلظت اولیه روی، pH محلول و زمان تماس بررسی شده است. بدین منظور، نانوکامپوزیت alginate-SBA-15 با روش کپسوله سازی به طریق تثبیت مزوپوروس SBA-15 درون یک ماتریکس پلیمری تهیه شده است. تعیین گروه های عاملی و مشخصه یابی سطح جاذب بدست آمده با استفاده از تکنیک های پراش پرتو ایکس (XRD)، میکروسکوپ الکترونی روبشی (SEM)، طیف سنجی مادون قرمز تبدیل فوریه (FT-IR) و تخلخل سنجی نیتروژن انجام شده است. عملکرد جذب جاذب alginate-SBA-15 طی آزمایشات ناپیوسته مطالعه شده است. به منظور توصیف ریاضیاتی فرآیند جذب، مدل های ریاضی سینتیکی و ایزوترم های تعادلی بر روی داده های آزمایش اعمال شده اند. مطالعه سینتیک نشان داد که مدل سینتیکی شبه درجه دوم تطابق بهتری با داده های تجربی نسبت به مدل شبه درجه اول دارد. بنابراین، آن نشان می دهد که هم غلظت یون های فلز روی و هم alginate-SBA-15در مرحله تعیین نرخ فرآیند جذب دخالت دارند. مقدار q_{max}برای جذب یون‌های روی بر روی جاذبalginate-SBA-15برابر$46.3\ mg\ g^{-1}$بدست آمده است. طبق تحلیل ترمودینامیکی، ماهیت فیزیکی و گرماگیر بودن فرآیند جذب یون‌های روی بر روی نانوکامپوزیت alginate-SBA-15 اثبات شد.

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