NA-ALGINATE BEADS OF CALCIUM / IRON-LAYERED DOUBLE HYDROXIDE FOR TREATING WATER CONTAMINATED WITH AMOXICILLIN ANTIBIOTIC

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ABSTRACT

The objective of this study was to prepare an adsorbent material from eggshells of chicken banished to the ambient as wastes to satisfy the ecological requirements of sustainable. The preparation process based on the extraction of calcium ions from eggshells and these ions must be reacted with iron to form nanoparticles of (Ca/Fe)-layered double hydroxides (LDHs) which immobilized as Na-alginate beads. Molar ration of calcium to iron, pH and dosage of LDH nanoparticles must be equal to 1, 12 and 5 g/100 mL to ensure that the prepared beads have highest ability to remove of Amoxicillin (AMOX) antibiotic with removal efficiency equal to 32% for operational conditions of Co=100 mg/L, beads dosage=0.5 g/50 mL, speed=200 rpm, pH=7 for 3 hrs. To increase this efficiency to ≥ 90%, best conditions must be time 90 min, pH 7, and beads mass 1.2 g/ 50 mL for C_o 100 mg/L at 200 rpm in the batch mode. The Pseudo second order has high capability in the description of such tests with coefficient of determination (R^2) ≥ 0.9924 and sum of squared error (SSE) ≤ 0.1287. Hence, the sorption of AMOX onto beads is governed by the chemisorption process. The reflections of XRD analysis proved the presence of (Ca/Fe)-LDH nanoparticles with size of 13.49 nm, calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$)

Key words: kinetic models, sorption, reactive material, eggshells, batch.

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حبيبات الجنيت الصوديوم للCa/Fe هيدروكسيد مزدوج الطبقات لمعالجة المياه الملوثة بالمضاد الحيوي الايموكسيسيلين

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باحث **استاذ**

قسم الهندسة البيئية– كلية الهندسة –جامعة بغداد– بغداد

المستخلص

ان الهدف من الدراسة الحالية هو تحضير مادة مازة من قشور بيض الدجاج المطروحة إلى البيئة المحيطة كنفايات لتلبية المتطلبات البيئية المستدامة. تعتمد عملية التحضير على استخلاص أيونات الكالسيوم من قشور البيض وهذه الأيونات يجب أن تتفاعل مع الحديد لتكوين جزيئات نانوية من (Ca/Fe) هيدروكسيدات مزدوجة الطبقات (LDHs) والتي تجمد على شكل حبيبات Na–alginate. يجب أن تكون النسبة المولارية من الكالسيوم إلى الحديد ودرجة الحموضة وجرعة الجسيمات النانوية LDH مساوية لـ 1 و12 و5 جم/100مل للتأكد من أن الحبيبات المحضرة لديها أعلى قدرة على إزالة المضاد الحيوي الايموكسيسيلين (AMOX) بكفاءة إزالة تساوي 32٪من أجل ظروف التشغيل لـ C_o=100 مجم/لتر، جرعة الحبيبات 0.5 جم/ 50 مل، السرعة 200 دورة في الدقيقة، درجة الحامضية=7 لمدة 3ساعات. لزيادة هذه الكفاءة إلى ≤ 90٪، يجب أن تكون أفضل الظروف هي الوقت 90 دقيقة، والحامضية 7، وكتلة الحبيبات 1.2 جم / 50 مل لـ C_o 100 مجم / لتر عند 200 دورة في الدقيقة. Pseudo second order لديها قدرة عالية في وصف هذه الاختبارات مع معامل 0.9924 (R^2) ومجموع الخطأ التربيعي 0.1287 (SSE). ومن ثم، فإن امتصاص AMOX على ألجينات الصوديوم تحكمه عملية الامتصاص الكيميائي. أثبتت انعكاسات تحليل XRD وجود جزيئات LDH– (Ca/Fe) النانوية بحجم 13.49 نانوميتر وهيدروكسيد الكالسيوم ($Ca(OH)_2$) وكربونات الكالسيوم ($CaCO_3$).

الكلمات المفتاحية: الموديلات الحركية، الامتزاز، المواد التفاعلية، قشر البيض، نظام الدفعة الواحدة

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INTRODUCTION

Pharmaceutical wastes were developing contaminants and abnormal fear as a result to their popular usage in the locations of living beings. During manufacturing and the use of many pharmaceuticals like antibiotics, chemotherapy agents, antidepressants, antipyretics, contraceptive drugs and analgesics, they are probably discharged to the aquatic systems without any effective remediation (7). Antibiotics are utilized extensively among these drugs as clinical medicines, animal growth promoter, and veterinary drugs. One of the major concern of rising rates in antibiotic tolerance to different types of bacteria because the frequent use of different antibiotic which led to an increasing number of pathogens which are unsusceptible to treatment with common antibiotics, hence this is real challenges on human health as well as other organisms (8, 20). The AMOX is widely used drugs for livestock and it can be released as well as accumulated in the natural water resources to form serious threat for human and aquatic ecology. Removal techniques that applied for effective removal of AMOX technologies were studied (10,23). Chemical and biological methods consider the familiar approaches that utilized in the disposal of pharmaceutical wastewater. Advanced oxidation, electro- and photo-chemical degradation, as well as electrocoagulation methods have acceptable effectiveness in the tackling of AMOX remaining in wastewater (16,31,5,26,22). Previous studies signified that the cost, efficacy and stability of mentioned methods can't explain the uncertainty in practical field. In opposite side, adsorption was appeared as technique that simple in operation, low in cost, flexible in application, and can treat wide range of contaminants; so, this method can consider more suitable for dealing with such problem (39,7,2). Various types of adsorbents like activated carbon, sawdust, clay, polymers, fly-ash and materials coated with nanoparticles have been developed to remediate water contaminated with organic contaminants (9,38,4,36,19). Activated carbon derived from "chicken feather which consisted of keratin" was tested to remove AMOX from simulated wastewater. Measurements certified that the surface area of manufactured carbon = 1838.86 m^2/g which used to eliminate AMOX with efficiency of 99.63% (22). Hydroxyapatite nanoparticles are formed from the reaction of calcium extracted from cement kiln dust and phosphate prepared from sludge of sewage. The final material named "Hydroxyapatite Coated Filter Cake (HAP-CFC)" can remove tetracycline (TC) from contaminated water with efficiency of 90% and maximum sorption capacity of 43.5 mg/g (17). Also Adsorption on algae were performed at different operational conditions with optimum pH=5 or AMOX solutions, agitation speed 200 rpm and concentration 50 ppm and the pseudo-second-order kinetic model was best fitted the experimental kinetic data of AMO onto algae biomass with a high coefficient of determination (0.97 -0.99) (3). Recently, studies were directed for manufacturing of LDHs that applied for fields of environment, magnetization and electrochemistry. LDHs are based on the connection occurred between divalent and trivalent metal ions in the presence of an anions. This work aims to prepare the Na-alginate from reaction of calcium (extracted from chicken eggshells) with iron to obtain LDH. Examination the adsorption of AMOX antibiotic onto prepared alginate and evaluation the influences of operational conditions on the performance of this composite sorbent are major goals of present batch study.

MATERIALS AND METHODS

Removal capacity: Eq. 1 is applied to find the quantity of AMOX attached to the alginate beads at equilibrium (q_e) based on the difference between initial concentration (C_o) and residual concentration (C_e) for certain volume of sample (V) and adsorbent mass (m) (36).

$$\boldsymbol{q_e = (C_o - C_e)\frac{V}{m}} \quad \textbf{(1)}$$

The removal percentage of AMOX (R) from contaminated water can calculate as follows:

$$\boldsymbol{R = \frac{(C_o - C_e)}{C_o} \times 100} \quad \textbf{(2)}$$

Kinetic models

The kinetic measurements obtained from experimental tests must be formulated theoretically using the following models (15):

Kinetic Pseudo first order model: is used for description the rate of sorption for solute from aqueous solution (33):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

Where k_1 is the rate constant of this model (1/min); q_e is adsorbed amount of solute at equilibrium and q_t is adsorbed amount of solute at time *t*.

Kinetic Pseudo second order model: supposes that the one layer of pollutant attaches to the surface of solid particles, sorption energy can't change for each sorbent and no interaction between sorbed species as explained in Eq. 4 (21):

$$q_t = \frac{k_2 q_e^2 t}{(1+k_2 q_e t)} \quad (4)$$

Where k_2 is the rate constant of sorption (g/mg min). ======**Intra-particle diffusion model:** can be written as follows (11):

$$q_t = k_{int} t^{0.5} + C \quad (5)$$

Where k_{int} is the adsorption rate constant of the intra-particle diffusion model (mg/g $min^{0.5}$), C is the value of intercept which gives an idea about the boundary layer thickness.

Materials

AMOX as powder was selected to be the target antibiotic and 1 L of distilled water contaminated with 1000 milligrams of this antibiotic had been prepared. This water (i.e. stock solution) was kept at room temperature and its acidity can be changed by drops of 0.1 M HCl and NaOH. For batch tests, stock solution was diluted to specific value of concentration for AMOX. The concentration of AMOX is determined by Ultraviolet-visible (UV)–visible spectrophotometer (Model Varian Cary 100conc., England) at wavelength of 270 nm (34,13).

Synthesis procedure

The preparation of Na-alginate is required to manufacture of LDH nanoparticles from reacting of Ca (extracted from chicken eggshells) with Fe. The LDH nanoparticles were manufactured by "Co-precipitation" method. The preparation process can be included:

1. The 20 g of shells mixed with 50 mL of solution (distilled water plus 35-38% hydrochloric acid) to extract the highest concentration Ca through agitated of mixture at 200 rpm for 3 hrs.
2. Specific mass of $Fe(NO_3)_3$ was dissolved in distilled water to obtain solution riched with iron.
3. The Ca/Fe nanoparticles in the shape of LDH can be prepared through mixing the two solutions obtained from previous steps under different values of pH like 7, 8, 10 and 12 in the flasks that agitated for 3 hours at 200 rpm.
4. Dissolving 2 g of Na-alginate in 100 mL of distilled water which thoroughly agitated by magnetic stirrer at room temperature for 24 h. This solution added to different quantities of (Ca/Fe) nanoparticles. The 0.1 M of $CaCl_2$ (dissolving 1 g of $CaCl_2$ in 100 mL of distilled water) for polymerization and beads formation using 10 mL syringe. The beads they have diameter approximately equal to 4 mm which cured in this solution for 24 h and then washed twice with distilled water and preserved in 5 mM of $CaCl_2$ (dissolving 0.278 g of $CaCl_2$ in 500 mL of distilled water) at 4°C for further use (12). The maximum removal efficiencies of AMOX were the indictors used to specify the best conditions of (Ca/Fe) molar ratio, dosage of (Ca/Fe)-LDH and pH of solution required for synthesis process.

Procedure for batch investigation

Kinetic behavior for AMOX removal by sorption onto beads of Na-alginate was specified through batch study. At specific C_o of AMOX, this study aims to determine the proper values of conditions (i.e. initial pH, contact time, mass of beads, and agitation speed) required to reach for suitable contact between the contaminant and prepared alginate. A set of flasks (250 mL) were used and certain volume of prepared contaminated water (V=50 mL) inserted in each flask for specific value of C_o. Beads with various masses (m) were mixed with aqueous solutions in the previous flasks which agitated for 3 hrs at 200 rpm. Thereafter, the beads of alginate separated from the solution by filter paper and C_e of antibiotic measured by UV–visible spectrophotometer. Conditions of batch operation were pH (3-12), C_o (100-250 mg/L), and sorbent dosage ≤1.2 g/50 mL.

RESULTS AND DISCUSSION

Manufacturing of Na-alginate beads

Specific volumes of HCl in the range from 5 to 20 mL were mixed with 50 mL of distilled water contained 20 gm of eggshells to specify

the best value of this acid that can extract the highest concentrations of calcium ions. Four beakers were prepared and contained different values of HCl acid; they must be thoroughly agitated for 3 h using magnetic stirrer. Atomic absorption spectroscopy must be used to determine the concentration of calcium ions in the solution of each beaker beyond filtration. The concentration of calcium ions extracted from chicken eggshells was not exceeded 200389 mg/L at highest volume of acid (i.e. 20 mL). Results signified that there is no significant difference between extracted Ca ions at 10 to 20 mL HCl; so, the 10 mL can utilize to prepare the aqueous solution with highest concentration of Ca^{+2}. The effects of solution pH, molar ratio of Ca to Fe, and mass of (Ca/Fe)-LDH nanoparticles on the manufacturing of Na-alginate were tested. The achieved maximum efficiency for AMOX removal from polluted water can be the criteria for identifying the suitable values for preparation conditions. The effect of water pH on the performance of prepared sorbent was plotted in Fig. 1(a) by changing it from 7 to 12 at (Ca/Fe) molar ratio 1 and (Ca/Fe)-LDH dosage 5 g/100 mL. Sorption has tested at alginate dosage 0.5 g/50 mL, C_o of AMOX 100 mg/L, initial pH=7, and agitation speed 200 rpm for 3 h. It is obvious that the maximum efficiency has occurred at pH 12 with value of 32%; however, the efficiency is decreased to 27.8% due to reduce of pH to 7 and this may be resulted from increasing the diameter of nanoparticles (29). Finally, the pH 12 was adopted in the manufacturing of present (Ca/Fe)-LDH –Na - alginate. Fig. 1(b) shows the effect of (Ca/Fe) molar ratios in the range (0.5 – 4) on the synthesis of Na-beads for pH 12 and dosage of (Ca/Fe)-LDH nanoparticles 5 g/100 mL under the same conditions of sorption test mentioned previously. This figure proves that the highest removal efficiency (32%) can be observed at molar ratio of 1. The decrease of efficiencies in comparison with the greatest one may be resulted from disorder of the LDHs structure of adsorbent or the change in the radius difference between Fe and Ca (24). The influence of nanoparticles dosage on the preparation of Na-alginate beads was investigated and measurements have been shows in Fig. 1(c). This dosage was changed from 1 to 6 g/100 mL Na-alginate at best values of initial pH and molar ratio of (Ca/Fe) specified from previous tests. This figure certifies that the increase of nanoparticles to alginate from 1 to 6 g was accompanied with remarkable increase in the removal efficiency of AMOX and addition of 5 g (Ca/Fe)-LDH per 100 mL can also considered suitable nanoparticles dosage with remarkable removal 32% of this antibiotic.

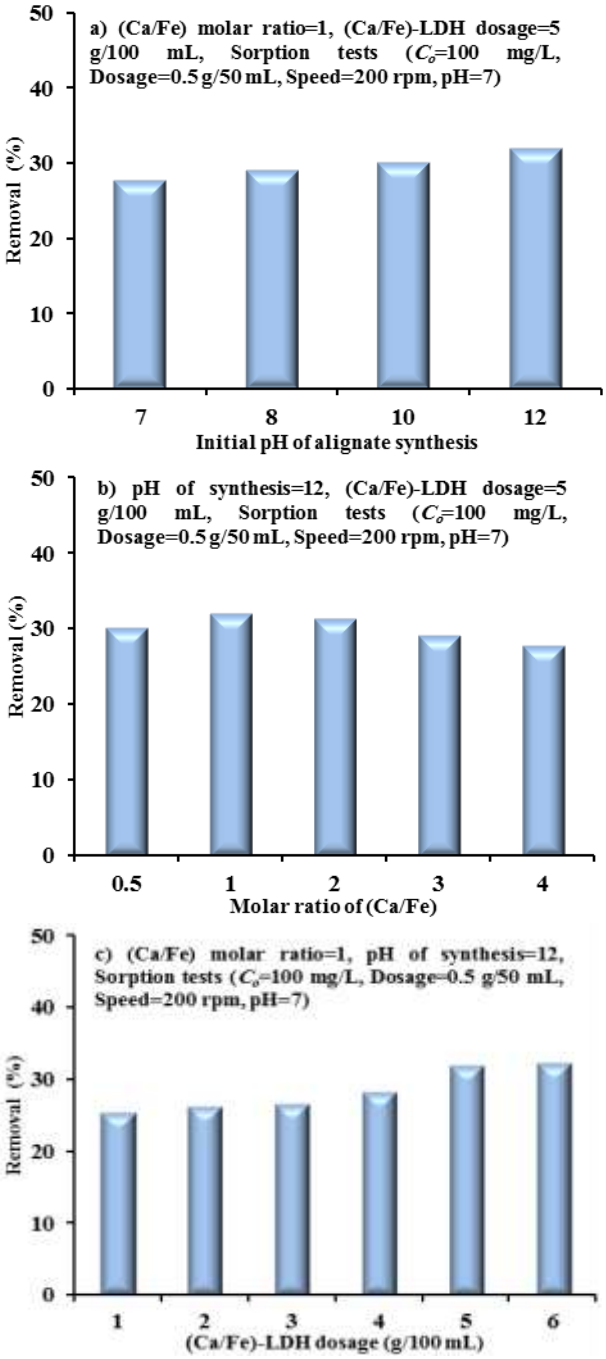


Fig. 1. Effects of a) initial pH, b) molar ratio of (Ca/Fe), and c) dosage of (Ca/Fe)-LDH nanoparticles on the preparation of Na-alginate beads used in the remediation of water contaminated with AMOX

The crystalline structure of Na-alginate beads was identified through application of X-ray diffraction (XRD) analysis as plotted in Fig. 2. Several reflections can recognize at certain intensities in terms of 2θ (degree) like 13.5, 20.4, 32.2, 43.6, and 45.1. These reflections represent the active sites available on the surface of Na-alginate that responsible of AMOX removal from aqueous solution. In comparison with "Joint Committee on Powder Diffraction Standards (JCPDSs)", the reflections have been corresponded to the (Ca/Fe)-LDH nanoparticles, calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$). The presence of (Ca/Fe)-LDH nanoparticles in the Na-alginate proves the success of formation of such component (28,32). The particle size of the produced LDHs was estimated by Scherrer equation as listed below (30)

$$\boldsymbol{D_s = \frac{K\lambda}{\beta_L \cos\theta}} \quad \textbf{(6)}$$

where D_s is the size of the Scherrer particle (nm), K is the form factor (approximated to a sphere, K = 0.91), λ is the X-ray wavelength used, β_L is the width at the peak half-height, and θ is the Bragg angle. Based on the mentioned values, the size of prepared nanoparticles was equal to 13.49 nm.

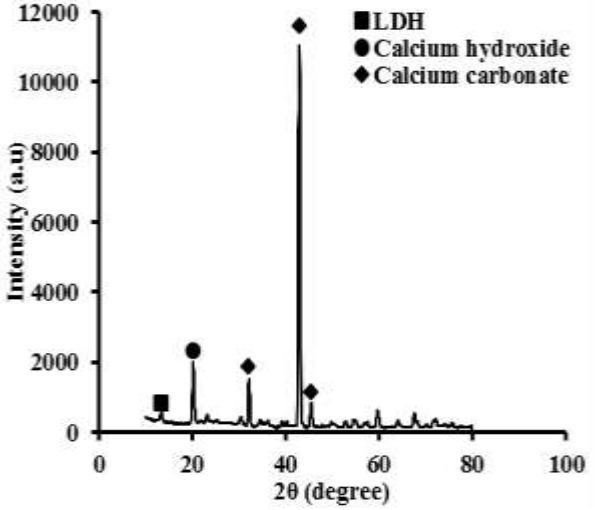
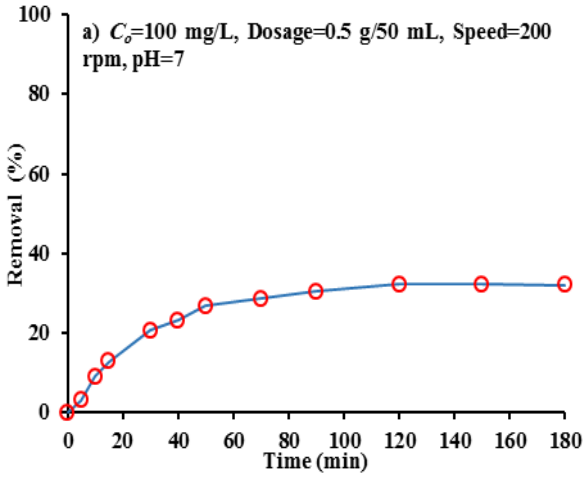


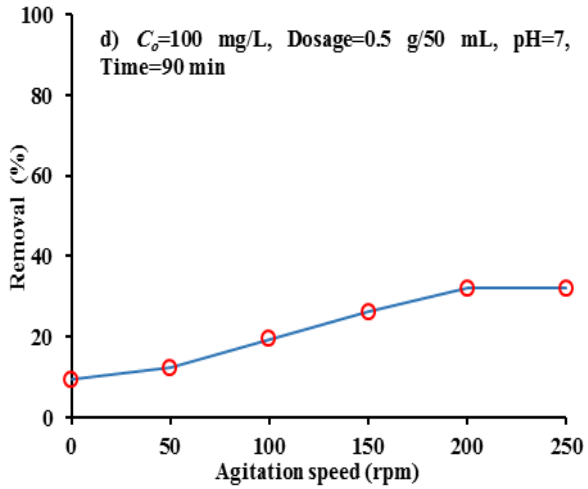
Fig. 2. The profile of XRD for crystalline structure of (Ca/Fe)-LDH-sodium alginate

Operating conditions

Fig. 3(a) illustrates the change in the removal of AMOX from contaminated water onto prepared beads of Na-alginate for agitation time ≤ 180 min at C_o 100 mg/L, initial pH 7, beads dosage 0.5 g/50 mL and shaking speed 200 rpm. The antibiotic is removed in the high rate for initial periods and this rate was reduced beyond 90 min due to decrease in the vacant sites available for sorption of AMOX molecules (18). This figure explained that the 90 min is acceptable to reduce 30.3% AMOX when C_o 100 mg/L; however, no remarkable variation in removal efficiency can recognize till 180 min. Fig. 3(b) shows that removal efficiency of AMOX onto alginate beads were changed dramatically from 32.1% to 12.72% for C_o 100 mg/L to C_o 250 mg/L when conditions were 90 min, pH indicate 7 with beads dosage 0.5 g/50 mL and 200 rpm shaking speed. It is expected that, at lower concentrations, all AMOX molecules have interacted with available binding sites and this can cause an increase in the removal efficiency; however, higher molecules for high concentration with fixed mass of beads can associate with reduce in this efficiency(1). Fig. 3(c) plots the relationship between the AMOX removal efficiency and values of initial pH that changed from 3 to 12. This figure signifies that the removal was low (≤14.9% at pH 3.0) and the competition of AMOX with H^+ ions may be the major reason for this behavior while the increasing of pH towards the neutral status may accompany with clear increment in the removal efficiency which has value not less than 32.1% at pH 7. The hydration and ionization of antibiotic can decrease at neutral condition and this can enhance the removal process through the hydrogen bonds and $\pi-\pi$ stacking effect. The same figure shows that there is evidence decrease in the removal efficiency due to change of solution towards the basic form and the efficiency has value greater than 18.2%. This reduction in efficiency with higher pH may result from the generation of OH^- which cause the attenuation in the hydrogen bonding. In most cases, amoxicillin has a positive charge when the solution pH lies below its isoelectric point which then shifts into negative charge as the solution pH rises above its isoelectric point. This phenomenon occurs due to the ionization of its functional groups, identified as carboxyl (pKa = 2.68), amine (pKa = 7.49) and phenolic hydroxyl (pKa = 9.63) (27). Fig. 3(d) certifies that the shaking speed with higher values has important role in the increasing the AMOX removal from contaminated water. The removal efficiency of AMOX was ≤ 9.4% for

stagnant aqueous solution; however, this efficiency can be increased drastically to be not less than 32.1% at 200 rpm for time 90 min, initial pH 7, beads dosage 0.5 g/50 mL and C_o 100 mg/L. This figure also illustrates that the increase of agitation to 250 rpm will not cause significant change in the removal efficiency. For higher shaking speed; accordingly, this can improve the transportation of AMOX molecules towards the solid phase recording to the suitable contact between the molecules and alginate beads. Fig. 3(e) shows the effect of alginate beads dosage on the removal efficiency of AMOX. It is obvious that the increase of this dosage from 0.1 to 1.2 g can increase the efficiency from lowest value (9.8%) to be not less than 90%. More alginate quantity means an increase in the vacant sites available for interaction with molecules of AMOX and this lead to significant increase in the removal efficiency of molecules (37).





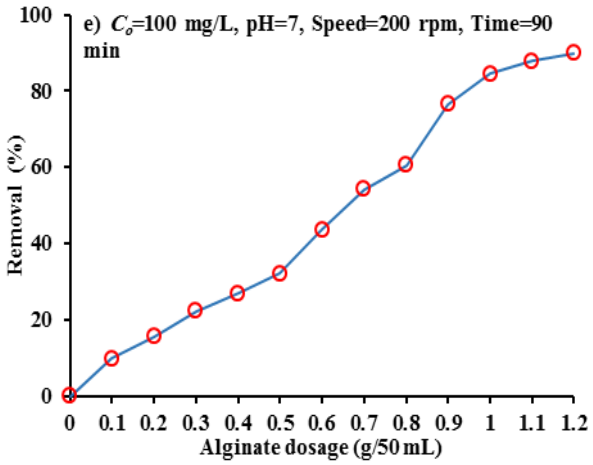


Fig. 3. Effects of a) contact time, b) initial concentration, c) initial pH, d) agitation, and e) sorbent dosage on the behavior of Na-alginate beads used for removal of AMOX from contaminated water

Kinetics of AMOX sorption

The sorption of AMOX antibiotic with the time using beads of alginate was monitored experimentally and formulated by kinetic models for various values of initial contaminant concentrations. The formulation process was achieved by fitting of measurements with Pseudo first and second order models (Eqs. 3 and 4) using "Non-linear Regression-Solver option" in Excel 2016. Table 1 lists the constants of kinetic models calculated from fitting; however, this table certifies that the pseudo second-order model has more ability in the representation of kinetic sorption process because $R^2 \geq 0.9924$ and SSE $\leq$ 0.1287.Also, the concurrence between measurements and kinetic models can be recognized from Fig. 4. Hence, the sorption of AMOX antibiotic onto alginate beads is governed by the chemical forces. Model for intra-particle diffusion (Eq. 5) was applied and constants of this equation related between q_t and $t^{0.5}$ have been calculated from non-linear regression fitting as listed in Table 1. Fig. 5 demonstrates that this relationship for AMOX is described by straight-lines which do not pass through the origin. So, this can clearly suggest that intra-particle diffusion is involved in the adsorption process but the rate-controlling step will not be represented. Additionally, the plots of intra-particle diffusion in this figure also display multi-linearity, signifying a controlled process of adsorption for AMOX through two or more simultaneous mechanisms. The slopes of lines

in "portion 1" are sharp; so, the removal rate of AMOX can be high in the initial sorption process due to the external surface adsorption because of the availability of vacant sites. Also, the slopes of lines in the "portion 2" are varied in gradual manner to be the intra-particle diffusion is rate-controlled. Finally, the "portion 3" represents the equilibrium stage that may be related to the slowing down of intra-particle diffusion because of low concentration of contaminant remaining in the water (25,35,14).

Table 1. Kinetic parameters for sorption of AMOX antibiotic onto prepared Na-alginate beads

Model	Parameter	Value
Pseudo-first order	$q_{eexp.}$ (mg/g)	3.5
	q_e (mg/g)	3.2828
	k_1 (min^{-1})	0.0298
	R^2	0.9899
	SSE	0.1554
Pseudo-second-order	q_e (mg/g)	4.0288
	k_2 (g/mg min)	0.0077
	R^2	0.9924
	SSE	0.1287
Intra-particle diffusion	Portion 1	
	k_{int} (mg/g min$^{0.5}$)	0.3958
	R^2	0.9519
	Portion 2	
	k_{int} (mg/g min$^{0.5}$)	0.199
	R^2	0.9329
	Portion 3	
	k_{int} (mg/g min$^{0.5}$)	0.1457
	R^2	0.873

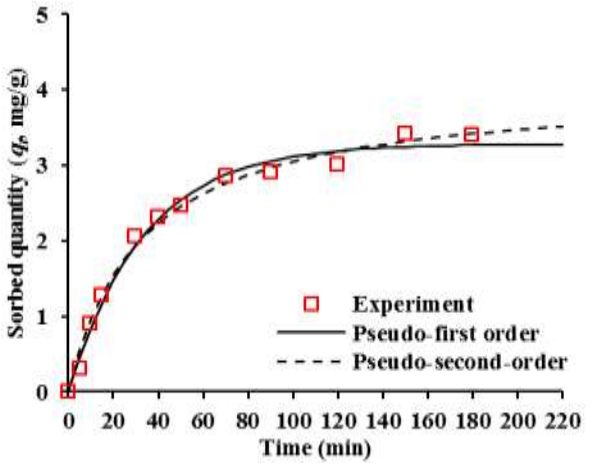


Fig. 4. Kinetic models for interaction of sodium alginate beads with water contained AMOX antibiotic

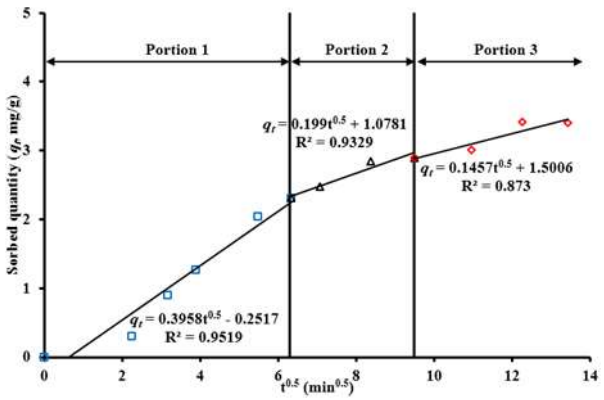


Fig. 5. Intra-particle diffusion model for interaction of Na-alginate beads with water contained AMOX antibiotic

CONCLUSIONS

Chicken eggshells have been applied to extract the Ca ions that must be mixed with iron ions to produce (calcium/iron)-LDH nanoparticles via precipitation procedure. The usage of these shells is compatible with principles of sustainability and green projects. The nanoparticles were immobilized with Na-alginate to obtain the beads that used for elimination of AMOX from aqueous solution. The best conditions for synthesis of beads were molar ratio of (Ca/Fe) = 1, pH = 12 and nanoparticles dosage = 5 g/ 100 mL. Results signified that the suitable operational conditions required to ensure the removal efficiency of AMOX > 90% were 90 min, pH 7, and dosage 1.2 g/ 50 mL for C_o 100 mg/L at 200 rpm. This process was chemisorption because of the application of Pseudo second order model. The XRD test for beads proved the formation of (Ca/Fe)-LDH nanoparticles, calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$).

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