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Study on dynamic adsorption and chemical regeneration of Cd(II) from textile effluents by new granular composite based on gluten

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Abstract. Composite granules (named Fe-PILMG) based on both an Algerian montmorillonite with iron and gluten as an inert binder are prepared and used in the elimination of cadmium by dynamic adsorption in fixed bed columns. This study is essentially focused on the adsorption of Cd (II) in dynamic mode on a fixed bed based on Fe-PILMG sorbent granules followed by a study on the chemical regeneration of these new saturated adsorbents. The various regeneration tests are carried out with NaOH solution. The experimental data on the elimination of Cd (II) (pH = 7, T = 20 ± 2°C) in dynamic mode reveal that this adsorption is considerably influenced by the flow rate (2 to 5 mL min-1), Cd (II) initial concentration (20 to 50 mg L-1), and bed height (5 and 15 cm) and that a modification of each of these parameters can strongly influence the efficiency of this process. The assessment of the experimental data is carried out using the Thomas, Yoon & Nelson and Bohart-Adams models. The fit of the experimental and modeled breakthrough curves indicates excellent applicability of the mathematical models studied which is confirmed by high values of the correlation coefficient for the Bohart-Adams model (R^2 = 0.99, model constants $N0$ = 634.87 mg L-1, kBA = 0.079 (L (mg min)-1), from Yoon and Nelson model (R^2 = 0.97, ζ = 413.03 min, KYN = 0.0049 min-1), Thomas (R^2 = 0.98, q0 = 49.03 mg g-1, KTH = 5.21 mL (mg. min)-1).

Keywords: adsorption; gluten; granule; pillared montmorillonite; regeneration

1. Introduction

Industrial activities generate a large variety of contaminated effluents which require an appropriate treatment before their release into the environment.

Today, water is considered a scarce resource that must be protected. However, increased industrial activity is increasing pressure on the planet's water resources. These activities generate a wide variety of toxic chemicals which join directly into the water cycle (Louadj *et al*. 2017). Heavy metals are increasingly contaminating water resources, particularly in surface and underground water sources located around industrial and residential areas.

Cadmium is a natural trace element that exists in bedrock, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels. Cadmium

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is found in nature at low concentrations. However, the exceeding concentration of cadmium in the environment is mainly due to discharges from various human activities (Elinder 1992).

It's considered one of the most bioavailable and toxic metals since it slowly accumulates in the tissues of living organisms throughout the food chain. Lakes characterized by low alkalinity (pH 6.0 to 6.5) often have a higher body or tissue load of cadmium. The increase in pH, alkalinity and water hardness decrease metal toxicity, as water temperature increases. Metals generally become more toxic as chemical activity increases causing metabolic rates in aquatic organisms. However, water hardness does not play an important role in controlling the bioavailability of metals but reduces their toxicities due to antagonistic mechanisms (Patrick 1993). Water loaded with heavy metals such as cadmium must undergo an adequate treatment using an efficient process in order to protect human health and the environment (Louadj *et al*. 2017, Satya *et al*. 2017, 2020a, b). Currently, there are various biological, chemical, and physical methods for removing Cd(II) from contaminated water, including those based on advanced oxidation processes (AOPs) and adsorption (Ahn *et al*. 2019, Chabane *et al*. 2017, Louadj *et al*. 2017).

Sorption (adsorption and/or biosorption) is one of the most effective technologies in the treatment of wastewaters. It has the advantage of removing these pollutants under relatively simple operating conditions and with minimal production of sludge. In this context, a cyanobacterium dried biosorbent (Aphanothece sp) has been used in the biosorption of cadmium (Satya *et al*. 2017).

Adsorption on modified bentonites is widely used in the removal of organic pollutants and/or heavy metals in aqueous media. However, for economic considerations, the choice of this adsorption process will essentially depend on the reuse of the adsorbents after their saturation. In this work, we propose the use of a new environmentally-friendly composite adsorbent based on modified montmorillonite and gluten. The effectiveness of these new granules prepared by dry granulation is compared with those of other conventional composite adsorbents. The proposed composite grains are characterized by high mechanical stability, low cost and high efficiency in removing organic pollutants and/or heavy metals (Ahn *et al*. 2019, Bleiman *et al*. 2010). Granulation is defined as a process of shaping powders to prepare granules, this technology is successfully implemented to aggregate small particles in the form of solid aggregates easily separable in aqueous solutions. In this context, gluten as biomaterial has become the preferred binder in granulation because it is inexpensive and non-toxic (Chabane *et al*. 2017, Louadj *et al*. 2017).

Gluten, which is a complex based on viscoelastic protein, is obtained by leaching from semolina or wheat flour and water. It is made up of 75 to 80 % protein, 5 to 7 % fat, 5 to 10 % starch, 5 to 8 % water and small amounts of mineral matter. Gluten proteins represent 80 % of the total grain protein (Wouters *et al*. 2017). These two types form the gluten network, the behavior of which greatly affects the rheological properties of pasta. Once hydrated, gliadins (which have plasticizing properties) give the dough its extensibility, viscosity and plasticity. The high tenacity and elasticity of the dough can be explained by the very specific properties of glutenins (Cui *et al*. 2017). These properties of glutenins have allowed to prepare solid granules and resistant of disintegration in effluents, which is practiced in industry. In the industrial field, the granular form is chosen and used in dynamic adsorption on fixed beds in columns to remove water-soluble pollutants (Bleiman *et al*. 2010, Chabane *et al*. 2017, Wouters *et al*. 2017). With these continuous treatments, the tests are continued until the granules of the bed are saturated with pollutants (Lu *et al*. 2011). In this context and due to the continuous flow of wastewater, the fixed bed based on Fe-PILMG granules could constitute an alternative of water pollution control and therefore a choice in different industrial applications.

In order to obtain basic engineering data, the continuous flow system on a fixed bed is generally an efficient process and suitable for large wastewater volumes and (sorption/desorption) cycles. Among the different adsorption process, the one based on a fixed bed column remains the most preferable because it can be carried out continuously for several successive adsorption-desorption cycles for long periods (Satya *et al*. 2020b).

Indeed, this fixed-bed reactor, as a simple model makes it possible to obtain lifetime of the bed and regeneration time. In general, the performance of fixed-bed column is studied by breakthrough curves, i.e., a representation of the pollutant-effluent concentration versus time profile in a fixed-bed column (Satya *et al*. 2020b). The mechanism of this adsorption is based on different phenomena, such as axial dispersion, resistance to film diffusion, resistance to intraparticle diffusion (for both pore and surface diffusion) and sorption equilibrium. The recycling process, which is based on a succession of adsorption and desorption cycles, offers substantial economic and environmental advantages (Louadj *et al*. 2017, Patel 2019). In this area, many researchers have taken an interest in the regeneration and reuse of saturated adsorbents due to the high cost of their production, their stabilization and their elimination (Patel 2019, Vakilia *et al*. 2019). Regeneration is therefore one of the most important characteristics of an adsorbent suitable for practical applications. An adsorbent can only be applied industrially if it can be reused in several operating cycles (adsorption - desorption) (Balsamo *et al*. 2013, Pietro *et al*. 2020, Satya *et al*. 2020b). Also, an extended contact between the adsorbent particles and the feed fluid, always leads to the creation of a thermodynamic equilibrium between the solid adsorbent and the solutes of the fluid phase. Under such conditions, the adsorption and desorption rates become equal and the net charge on the solid can no longer increase. It is therefore advisable to regenerate the saturated sorbent or to replace it (Jatta *et al*. 2019).

In some applications, it may be more economical to replace the adsorbent after its saturation, especially when the adsorbent is of low cost. In the majority of applications, the elimination of adsorbents as waste is not an economical option and, therefore, the regeneration is carried out either in situ or outside the adsorption reactor insofar as the adsorbents could be reused again. Therefore, traditional chemical regeneration remains attractive and deserves to be reconsidered. It can be carried out quickly in situ and without degrading the pore structure observed by some with the other methods (Lu *et al*. 2011). In this field, various regenerating inorganic and organic were evaluated to treat some modified montmorillonites (Lu *et al*. 2011, Patel 2019). Numerous studies have focused on the elimination of heavy metals by using adsorbents based on natural and/or modified montmorillonite from aqueous solutions (Lu *et al*. 2011, Vakilia *et al*. 2019). However, few studies report information on the recycling and regeneration of saturated adsorbents.

This study is therefore focused on the following points: (a) Preparation of a new generation of composite granules denoted “Fe-PILMG” based on an Algerian montmorillonite with iron pillars (Fe-PILM) and gluten (G) , (b) Dynamic adsorption tests on fixed beds by examining the effects of various operational conditions such as flow rate, bed length and initial concentration of Cd(II)), (c) Appropriate modeling and exploitation of the various breakthrough curves, (d) Regeneration test of saturated Fe-PILMG granules by chemical desorption in continuous mode on columns.

2. Materials and methods

2.1 Preparation of new granular composite adsorbent

The starting bentonites supplying the montmorillonite (Mt) comes from the Maghnia deposit

(Algeria). Its chemical and mineralogical compositions are already presented (Ararem *et al*. 2011). The used Gluten (G) consists of 75 to 80 % protein, 5 to 7 % lipids, 5 to 10 % water and small amounts of mineral matter. Gluten proteins represent 80 % of the total grain protein (Wouters *et al*. 2017). The two basic materials (iron pillared Mt and G) are used in the formulation in order to prepare a new generation of granules denoted Fe-PILMG.

The fraction of montmorillonite of size < 2 μm is converted into saturated form or sodic homoionic montmorillonite (Na-Mt). This is first obtained by treatment with 0.1 M NaCl solution followed by several successive washes with deionized water (Resistivity > 18 MΩ cm, Dissolved organic carbon less than 0.2 mg L-1) at room temperature (20 ± 2°C) until the supernatant is free of chlorides. The obtained product is designated hereafter by Na-Mt (Khalaf *et al*. 1997).

The Iron pillaring agent is prepared as follows (Bouras *et al*. 2010): a 0.75 M NaOH solution is slowly added drop by drop (0.6 mL mn−1) to 0.43 M FeCl3•6H2O solution with vigorous stirring to obtain a final solution with a final concentration of 0.2 M and (OH/Fe) molar ratio equal to 2 (Zermane *et al*. 2013).

The pillaring agent, named hereafter (PCBF), is left to age for 10 days at room temperature (20 ± 2°C). After aging, the resulting solution was reacted with 0.5% aqueous suspension of Na-Mt at a ratio OH/Na-Mt of 5 mmol g−1 (Cheknane *et al*. 2012), and left to react under vigorous stirring at room temperature (20 ± 2°C). After filtration and washing several times with deionized water, obtained solid corresponding to iron-pillared montmorillonite designated hereafter by Fe-PILM is dried at 40°C for at least 72 h, ground, and then stored in dark bottles away from light (Ararem *et al*. 2011).

The used gluten (noted G) is extracted from wheat by continuous treatment with a concentrated solution of NaCl (25 g L-1). This chemical treatment is continued until the liquid becomes transparent. Gluten obtained by drying at room temperature (20 ± 2°C) for a period of 48 h, and stored in a dark bottle before its use in the granulation process by compacting.

The granulation process is done by controlling the sputum mixture, as it passes through two rotating wheels in the opposite direction at a speed of 2.5 rpm for 24 s. 12 g of powder mixture of Fe-PILM and 8 g of G at a weight ratio (6/4, w/w) are injected into the compacting granulator. The resulting granules of size (800 to 1200 µm), are used in the dynamic adsorption tests on Cd(II) on a fixed bed based on Fe-PILM in columns. A stock solution (1 g. L-1) of cadmium nitrate (Chemical formula: $Cd(NO_3)_2$, Molecular weight: 236 g. mol−1, Purity: 99%) is prepared by dissolving the appropriate quantity in deionized water into brown flasks. The preparation is carried out at room temperature (20 ± 2°C), shaken for several hours and then filtered through a Sartorius cellulose nitrate membrane (0.45 μm) before use. All the experimental solutions are obtained by successive dilutions in deionized water at room temperature (20 ± 2°C) and are stored at 4°C in the dark.

2.2 Dynamic adsorption and regeneration tests on column

Adsorption and regeneration experiments on a column are carried out in a Pyrex glass column (Diameter: 1 cm, Length: 15 cm). This column is filled with 6.22 g of Fe-PILMG granules with a particle size between 800 and 1200 μm. For a uniform distribution of the liquid and to avoid possible flotation of the adsorbent granules, the adsorbent bed is limited by two small sieves.

As shown in Fig. 1, the Fe-PILMG granules prepared are weighed, introduced into the column and compacted as uniformly as possible with a rigid and thin rod. All the experiments are carried out by pumping a Cd(II) solution in continuous ascending mode through the fixed bed with a

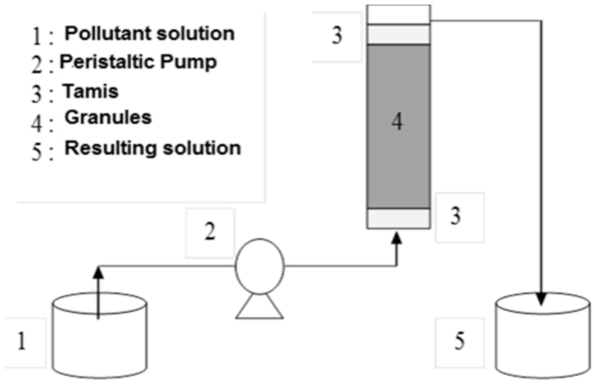

Fig. 1 Experimental method used in the dynamic adsorption of Cd(II) on a fixed bed based on Fe-PLIMG granules

Table 1 Hydrodynamic characteristic of the column adsorption experiments

h (cm)	m_T (g)	V_T (cm^3)	ρ_d (g cm^{-3})	ε	V_p (cm^3)
5	1.40	3.92	0.356	0.69	2.70
15	6.22	11.77	0.528	0.55	6.47

peristaltic pump (ISMATEL 829B). In these different tests, the effects of concentration (ranging from 20 to 50 mg L-1), bed height (5 to 15 cm), flow rate (2 to 5 ml min-1) are studied. Samples are taken from the top of the column at regular intervals and the residual cadmium concentrations are determined by atomic absorption at 228 nm using a Shimadzu AA-7000 series atomic absorption spectrometer. All the experiments are conducted at optimal pH = 7 and room temperature (20 ± 2°C) (Louadj 2019). The breakthrough curves obtained at different operating parameters are expressed by the evolution of C/C0 as a function of time.

The dynamic adsorption parameters were calculated using the following equations.

The means volumic mass ρ (g cm^{-3}) of the porous medium is calculated using the following relationship:

$$\rho = {}^{m_T}/_{A.h} \tag{1}$$

where A (A = 0.785 cm²) is the surface of the column; m_T (g) is the total introduced mass of Fe-PILMG; h (cm) is the desired bed height.

The mean porosity ε of the porous medium is calculated as follows:

$$\varepsilon = 1 - {}^{\rho}/_{\rho_s} \tag{2}$$

where, ρs is the volumic mass of solid granules (equal to 1.18 g .cm^{-3}). The volume pore Vp (cm^3) is expressed by:

$$V_p = V_T.\varepsilon \tag{3}$$

where, V_T is the total bed volume (cm^3).

The hydrodynamic conditions of the various dynamic adsorption experiments on a column are summarized in Table 1.

A useful parameter for designing dynamic adsorption processes is the degree of use (η) of the bed. This was expressed earlier by equation (Eq. (4)).

$$\varepsilon = 1 - {}^{\rho}/_{\rho_s} \tag{4}$$

q_r and q_s : adsorption capacities at rupture and saturation (mg. g^{-1});
V_f : volume of effluent until the first appearance of the solute in the effluent (cm^3);
V_r : volume of effluent at rupture (cm^3);
V_t : volume of treated effluent until the solute concentration at the outlet equals that of the inlet (cm^3).

The regeneration tests of the saturated granules are carried out by continuous rinsing the Fe-PILMG granules with NaOH or HCl solutions. These tests are carried out under the following operating conditions: h = 15 cm, Q = 2 mL. min^{-1}.

After each desorption cycle, the bed is washed with deionized water until the pH of the effluent is equal to that of the input solution. Cadmium concentrations in elution water samples are measured by atomic absorption.

The column adsorption capacity in each cycle is calculated from the breakthrough curve and the regeneration efficiency (RE) is calculated according to the following equation:

$$RE(\%) = \frac{q_i}{q_0} \times 100 \tag{5}$$

where q0 and qi (mg. g^{-1}), represent the capacity of the fresh column and that of the regenerated column, respectively.

2.3 Mathematical models for breakthrough curves

Several mathematical models, such as those of Thomas, Yoon-Nelson and Bohart-Adams, have been developed and widely applied to fit and adjust the experimental data of dynamic column adsorption tests in order to predict the concentration-time profiles and breakthrough curves. In this study, these models are used in order to choose the most suitable model that best describes the breakthrough curves and therefore to assess the maximum capacity of the column They can be obtained from a plot of C/C_0 against time (t) using the non-linear regression method.

2.3.1 Thomas model

In column performance theory, the Thomas model is the most widely used (Thomas 1944). In practice, this simple design model is used for any type of balance it ignores both the resistance to intra-particle mass transfer and the external resistance (fluid film) by supposing that the solute is adsorbed directly on the surface of the solid. This means that the adsorption rate is controlled by the surface reaction between the adsorbate and the fraction of fresh adsorbent. Thomas equation can be expressed as:

$$\frac{C}{C_0} \cong \frac{1}{1 + exp\left(\frac{K_{Th} q_0 M}{Q} - K_{Th} C_0 t\right)} \tag{6}$$

where the following parameters represent:
K_{th} : Constant of Thomas (mL. min^{-1} mg^{-1}),
q_0: Maximum capacity of effluent on the adsorbent surface (mg g^{-1}),
Q : Volume flow rate of effluent (mL. min^{-1}),
m : mass of granules (g).

2.3.2 Yoon and Nelson model

This model is based on the assumption that the rate of decrease in adsorption is proportional to both Yoon and Nelson have developed a theoretical model (Yoon *et al*. 1984) to predict breakthrough curves during dynamic adsorption in the gas phase. This model is based on the assumption that the rate of decrease in adsorption is proportional to both the retention and the breakthrough of the adsorbate. The equation of the Yoon and Nelson model is written as follows:

$$\frac{C_t}{C_0 - C_t} = \exp(k_{YN} t - \tau\, k_{YN}) \quad (7)$$

where the following parameters represent:

k_{YN} : Reaction constant;

τ: Time at which 50% of the solute entering the column is discharged (min).

2.3.3 Bohart-Adams model

The Bohart-Adams model assumes that the desorption rate is a function of the adsorption capacity and the concentration of metal ion (Chen *et al*. 2012). This model is illustrated by the following equation.

$$\ln\left(\frac{C_0}{C} - 1\right) = \ln\left(e^{\frac{kN_0h}{u}} - 1\right) - kc_0t \quad (8)$$

where C_0 and C represent the initial concentration of effluent and concentration at time t, respectively (mg. L^{-1});

k : Rate constant (L•mg^{-1}•min^{-1});

N_0: Volumetric adsorption capacity (L);

h : Bed height (cm);

t : Service time of column (min).

3. Results and discussions

3.1 Influence of parameters of fixed-bed column

After a series of dynamic adsorption tests on fixed-bed columns, three models are applied to adjust the experimental data to describe the fixed-bed column behavior.

3.1.1 Effect of different bed depths

The corresponding results presented in Fig. 2 show that the two saturation and rupture times increase with the increase in the depths of the bed. The adsorption of Cd(II) increases in the same direction as the depths of the bed. A higher bed depth provides both higher active sites and sufficient contact time.

The study of the influence of depths bed shows that the saturation time depends on the bed depths. The breakthrough time is of the order of 15 and 260 minutes, while the saturation time is around 300 and 800 min obtained with the two depths of the bed of 5 and 15 cm, respectively. The corresponding adsorption parameters of Cd(II) are presented hereafter in Table 2.

3.1.2 Effect of effluent flow rates

The results in Fig. 3 show that an increase in flow rate accelerates the breakthrough and

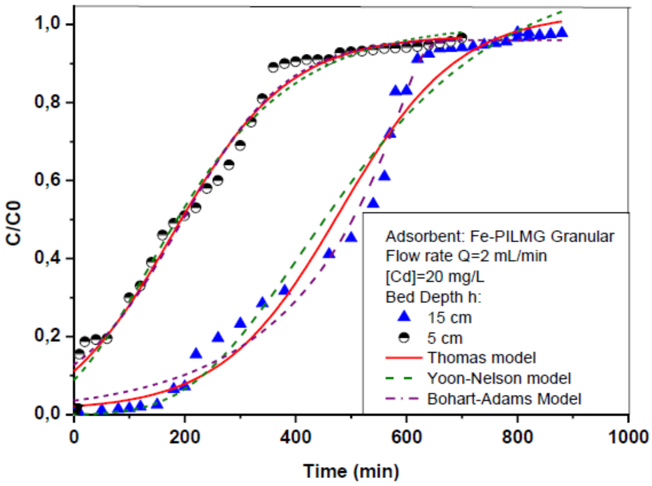

Fig. 2 Effect of various bed depths on the breakthrough curve of Cd(II) adsorption on Fe-PILMG

Table 2 Cd(II) adsorption parameters as a function of operating conditions

Parameters	Volume (mL)	Rupture time (min)	Saturation time (min)	Q (mg g^{-1})
Bed depths h (cm)				
5 (m = 1.40 g)	600	15	300	12
15 (m = 6.22 g)	1600	260	800	32
Flow rate Q (mL min^{-1})				
5	1600	85	320	32
2	1600	260	800	32
C_o (mg L^{-1})				
50	1000	150	500	50
20	1600	260	800	32

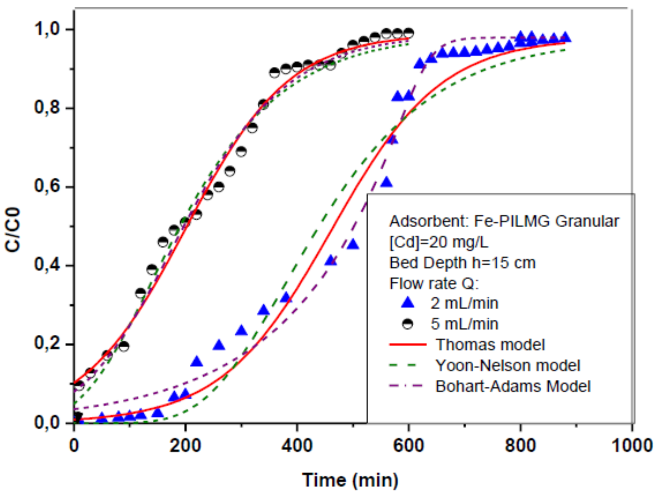

Fig. 3 Effect of flow rate on dynamic adsorption of Cd(II) on Fe-PILMG granules

therefore the saturation of the bed. When the flow rate increases the saturation time decreases. Similar results are obtained by various authors having worked on the dynamic adsorption in columns of heavy metals on various granulated adsorbents (Ahn *et al*. 2019, Bleiman *et al*. 2010, Cheknane *et al*. 2012, Satya *et al*. 2020b). This can be explained by the fact that at lower flow rates, the residence time of the adsorbate is longer and therefore the adsorbent gets more time for better diffusion in porous system of the material. On the other hand and for higher flow rates, the adsorption capacity is lower since the insufficient residence time and the adsorbate leave the column even before the equilibrium of the time.

For the different flow rates tested, the evolution of the concentration at the outlet as a function of time shows that the rupture times are shorter and the slope of the saturation is important when the feed flow is high. The saturation time increased from 320 to 800 min when the flow rate varies from 5 to 2 mL min-1.

This can be explained by the fact that at low flow rate, the adsorbate has a longer residence time and therefore the adsorbate has more time to diffuse into the porous system of the adsorbent material. At higher flow rates, the obtained adsorption capacity is lower due to an insufficient residence time and therefore less diffusion into the pores of the adsorbent.

These results are consistent since the adsorbed quantities of Cd ion increase in the same direction as the feeding speed and the rapid saturation of the bed. The corresponding results, presented in Table 2, are in perfect agreement with those previously observed by Cheknane *et al*. (2012) and Ararem *et al*. (2011) and Satya *et al*. (2020b).

The removal of cadmium in aqueous media has been studied previously using silicone granules (Cheknane *et al*. 2012), mixtures of iron pillared layered montmorillonite and goethite (Ararem *et al*. 2011) and dried biosorbent of cyanobacterium Aphanothece sp (Satya *et al*. 2020b).

The results of all these studies seem to be in perfect agreement with ours. However, the best Cd removal was obtained at low inlet Cd concentration, high adsorbent bed height and low effluent flow rate.

3.1.3 Effects of Cd(II) inlet concentration

An increase in the concentration of the effluent from 20 to 50 mg. L-1, the breakthrough reaches its saturation point more quickly. Indeed, for a higher effluent concentration, the driving force of mass transfer increases, which quickly saturates the binding. In such conditions, the breakthrough curves become

Fig. 4 shows the breakthrough curves obtained for the different concentrations studied.

Examination of these curves shows that, for a high initial concentration of Cd(II) (C0 = 50 mg. L-1), the breakthrough time and the adsorption equilibrium appear more quickly. Under such conditions and due to the significantly higher mass transfer, the active sites of Fe-PILMG granules saturate more quickly. On the other hand, for a low initial concentration of solute (C0 = 20 mg. L-1), the diffusion becomes slower, which results in a slowing down of the mass transfer and therefore a late appearance of the rupture of the curves. The corresponding results are presented in Table 2.

The degree of column utilization η may be defined as the ratio of mass adsorbed at breakthrough to the mass adsorbed at complete saturation.

By plotting the evolution of the degree of utilization η in function of the feed flow rate Q, we can observe that, the degree of column utilization lies in the range 10% for cadmium ion adsorption. Further, Fig. 5 shows that, the usage of high flow rates means that at break times the part of the bed used throughout the service time remains low. This may be due to lesser contact

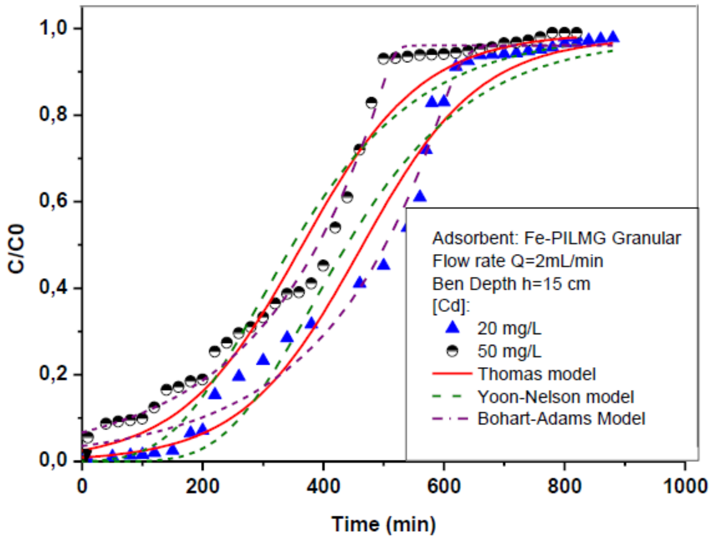

Fig. 4 Effect of Cd(II) concentration on the breakthrough curve adsorption on Fe-PILMG

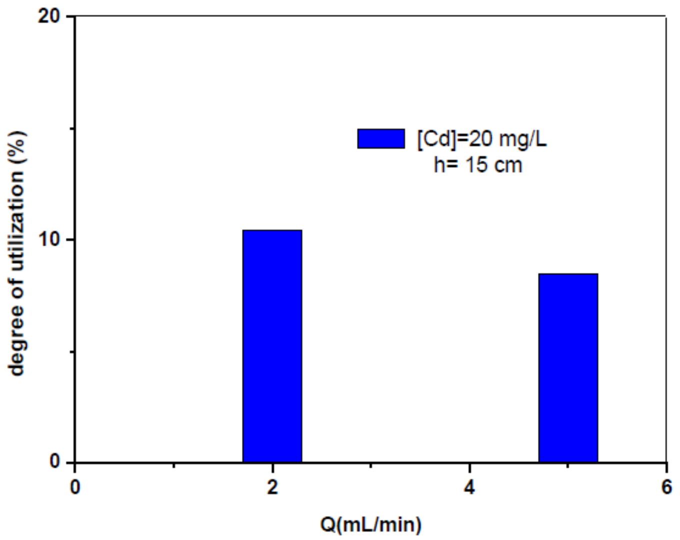

Fig. 5 Degree of utilization of Fe-PILMG granules bed

Table 3 Thomas model parameters under different operating conditions

C (mg L^{-1})	Q (mL min^{-1})	h (cm)	Thomas model		
			q_0 (mg g^{-1})	K_{TH} (mL (mg min)$^{-1}$)	R^2
20	5	15	34.70	4.652	0.98
20	2	15	49.03	5.213	0.98
20	2	5	30.05	4.931	0.98
50	2	15	58.25	2.005	0.97

Table 4 Yoon-Nelson model parameters under different operating conditions

C (mg L^{-1})	Q (mL min^{-1})	h (cm)	Yoon and Nelson model		
			τ (min)	K_{TH} (mL (mg min)$^{-1}$)	R^2
20	5	15	141.546	20	5
20	2	15	413.031	20	2
20	2	5	131.792	20	2
50	2	15	293.075	50	2

Table 5 Bohart-Adams model parameters under different operating conditions

C (mg L^{-1})	Q (mL min^{-1})	h (cm)	Bohart-Adams model		
			N_0 (mg L^{-1})	K_{TH} (mL (mg min)$^{-1}$)	R^2
20	5	15	99.948	20	5
20	2	15	634.877	20	2
20	2	5	214.076	20	2
50	2	15	525.77	50	2

Table 6 Used concentrations of eluted Cd ion

		Cd concentration (mg L^{-1})	$V_{éluent}$ (mL)
NaOH (M)	0.5	186	15
	1	312	32
HCl (M)	0.5	66	56
	1	124	37

time of the cadmium with granules which require longer time for equilibrium and thus, inhibiting the utilization of column capacity.

The value of η is maximum for Q = 2 mL. min-1, the low flow rate obviously leads to better utilization of column capacity at a time. Thus, these results have shown that the columns can be used to remove cadmium ion from aqueous solutions, adsorbed at a slow flow rate in column thus leading to a better degree of column utilization.

3.2 Modeling of the breakthrough curves

Dynamic adsorption tests in a column on a fixed bed are used by modeling the rupture curves to assess the adsorption performance under different operational conditions.

The estimated values of Thomas constants KTH and q0 determined using Eq. (6) are listed in Table 3. The corresponding results show that the constants are significantly influenced by the flow rate, the bed height and the Cd(II) initial concentration.

The fit of the experimental and modeled breakthrough curves indicates an excellent applicability of the Thomas equation which is confirmed by high values of the square correlation coefficient (R^2 > 0.97).

The Yoon and Nelson model is adjusted to study the breakthrough behavior of Cd(II) ions onto

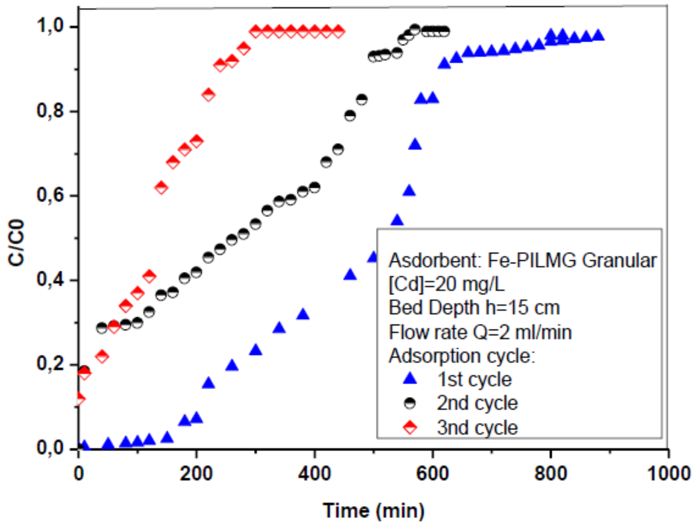

Fig. 6 Adsorption cycles of Fe-PILMG after three successive regenerations cycles

Fe-PILMG adsorbent grains. The Yoon and Nelson constant, τ (the time required for 50 % MG breakthrough) and k_{YN} (a rate constant) were obtained using a non-linear regression analysis according to the Eq. (7) and the corresponding results are listed in Table 4. The values of kinetic constants are significantly influenced by the flow rate, the initial ion concentration and the bed height of granules. However, a modification of one of these parameters can greatly change the Yoon and Nelson constants (τ, K_{YN}). The corresponding results in Table 4 clearly show that the correlation between the experimental and predicted values deviates slightly.

The Bohart-Adams model assumes that the desorption rate is a function of the adsorption capacity and the concentration of metal ions. Table 5 shows the different values of the parameter of the model parameters N_0 as well as the other calculated statistical parameters. These results show that the value of kinetic constant k decreases, with a decrease in the height of the bed and in the concentration of Cd (II). The parameter N_0 decreases with the increase in the concentration of Cd(II) concentration, the flow rate and the height of the bed of the column since the values of the coefficient R^2 are very satisfactory which are of the order of 0.99.

3.3 Regeneration studies

According to the regeneration tests, it is observed that the 1 M NaOH solution is an effective regenerator in desorption of Cd(II). Fig. 6 illustrates the adsorption cycles of Cd(II) onto Fe-PILMG granules. The corresponding breakthrough curves become steeper and faster for each successive cycle. Table 6 shows the maximum concentrations of Cd(II) obtained for each acid or base concentration used.

The values in the Table 6 show clearly the efficiency of desorption of Cd(II) ions from the NaOH solution (1 M). The choice of this eluent is based on the sorbent recovery criterion and therefore for the possibility of regenerating the adsorbent bed for possible future uses.

In practice, the granules bed is regenerated and reused in three successive adsorption-desorption cycles. Breakthrough curves expressing the adsorption-desorption cycles of Cd(II) are presented in Fig. 6.

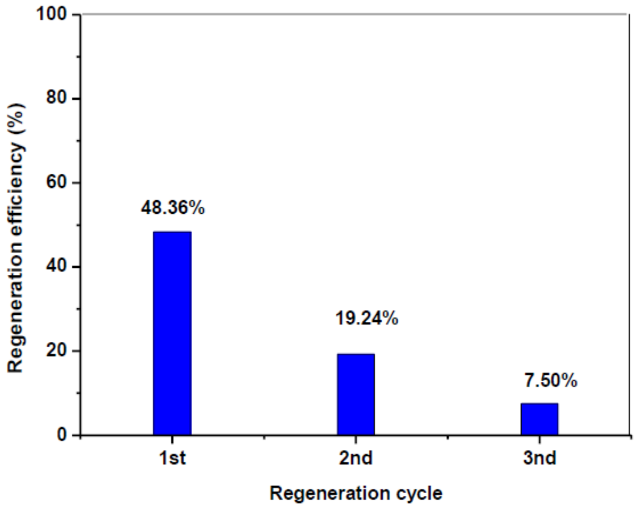

Fig. 7 Regeneration efficiency of Fe-PILMG granules after each regeneration cycle

These curves show a reduction in service time from 110 to 5 min in the second and third cycles. The reduction of service time as a function of the adsorption-desorption cycles could be due either to the inaccessibility of the sites occupied by Cd(II) during the previous cycle, or to a partial destruction of the active surfaces caused by the eluent.

This RE parameter of Fe-PILMG granules after each regeneration cycle is estimated from the equation (Eq. (5)). The corresponding results are presented in Fig. 7.

The observed results show that, the efficiency of the saturated Fe-PILMG granules continued after regeneration until the third cycle. However, this adsorption capacity dropped to 19.24 and 7.5 % from the 2nd and 3rd cycles, respectively.

The results show that the regeneration efficiency of the granules after the first cycle is only 48.36%, a small part of the granules has been regenerated, due to the removal of low adsorbed cadmium on Fe-PILMG. It is reasonable to admit that not all ions were achieved by regeneration. This performance impairment is due to the obstruction of granules porosity by adsorbed cadmium ions, thus reducing the adsorption capacity. Ions that are probably chemisorbed to the surface and pores of Fe-PILMG granules are difficult to desorb, which has a real influence on regeneration efficiency. This problem worsens when the number of cycles increases.

4. Conclusions

The aim of this study is to evaluate the performance of this new generation of Fe-PILMG granules in the elimination of cadmium by dynamic adsorption on a fixed bed in columns.

The results obtained make it possible to give the following conclusions:

The breakthrough time and the adsorption capacity increase with increasing bed height and decreasing both the initial concentration of the solute and the feed rate of the bed.

Columns with bed heights of 5 and 15 cm adsorb approximately 12 and 32 mg. g^{-1} of cadmium, respectively. The breakthrough time and exhaustion time increased as the depth of the bed increased.

The sorption dynamics are better described by the Adams-Bohart model than by the Thomas and Yoon and Nelson models.

The rupture curves made it possible to determine the parameters linked to the models used.

The Fe-PILMG granules bed saturated with cadmium ions seem to be better regenerated by NaOH (1 M) solution.

The capacity of the Fe-PILMG sorbents in the adsorption of Cd(II) decreases slightly after three successive cycles of adsorption-desorption, showing a real possibility of regeneration of these new granular adsorbents.

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