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Granular inorgano-organo pillared clays (GIOCs): Preparation by wet granulation, characterization and application to the removal of a Basic dye (BY28) from aqueous solutions

Benamar Cheknane[a,b,c], Omar Bouras[c], Michel Baudu[a,*], Jean-Philippe Basly[a], Aicha Cherguielaine[c]

[a] Groupement de Recherche Eau Sol Environnement (EA 4330), Université de Limoges, 123 Avenue Albert Thomas, 87060-Limoges, France
[b] Centre de Développement des Energies Renouvelables, B.P.62, Route de l'observatoire, Bouzaréah, Alger, Algeria
[c] Département de Chimie Industrielle, Université Saad Dahlab, BP 270, 09000-Blida, Algeria

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ABSTRACT

The aim of the study was to prepare resistant and spherical inorgano-organo pillared clays (GIOCs) granules for wastewater treatment using a new and simple method named high-shear wet granulation. To optimize the preparation method, the effects of the main process parameters, such as binder concentration, liquid to solid ratio and impeller speed on granule properties (size distribution, friability and disintegration tests) were investigated. Experimental results showed that the granulation of inorgano-organo pillared clays (PIOCs) with industrial Silicone is significantly influenced by the binder concentration, the liquid to solid ratio (H %) and the impeller speed (N). A modification of these parameters can greatly alter the characteristics of the granules. The impact of wet granulation on the kinetics and adsorption capacities of GIOCs was estimated using Basic Yellow 28 as model pollutant. Kinetic studies reveals that BY 28 adsorbed faster on PIOCs ($k_1 = 7.40 \times 10^{-2}$ min^{-1}) than on granular forms. Results best fitted the pseudo-first-order kinetic model. It was also found that the adsorption kinetic is directly related to the surface diffusion of prepared GIOCs. The adsorption equilibrium data were analyzed by the Langmuir and Freundlich models using non-linear regression. The best fit to the data was obtained with the Langmuir isotherm. The highest adsorption capacities ($Q_{max} = 514$ mg/g; pH 6) for GIOCs were obtained for the finest forms (300–400 μm).

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1. Introduction

Due to their low cost, high adsorption capacity and operational simplicity, pillared clays (PILCs) had become an important and widely used adsorbents in the last decades. These solids are obtained from clays by introducing large polyoxycations into the interlayer region; the compounds used as pillaring agents are frequently Al, Ti, Cr and Fe polymeric derivatives [1–4]. The structural diversity of organic–inorganic modifications in PILCs offer the potential to increase the sorption capacities and numerous studies have been directed towards the use of PIOCs for the elimination of metals, organic pollutants or dyes from aqueous solutions [5–8].

Agglomeration of powder inorgano-organo pillared clays (PIOCs) by wet granulation to obtain granular inorgano-organo pillared clays (GIOCs) could increase the physical properties (bulk density, porosity, hardness, compressibility) thus enhancing the field of applications of the resulting solids in water treatment. High-shear wet granulation is a size enlargement process widely used in various industries. During this process, the powder is blended by intense mechanical agitation with an impeller followed by the addition of a liquid binder. Continuous agitation throughout wet massing leads to the formation of a granules and their growth result of mobile-liquid bonds formed between primary particles [9]. The granulation, dependent of the physico-chemical properties of primary particles, the binder solution and the operating conditions can be described by three mechanisms: wetting and nucleation, followed by consolidation and coalescence and finally attrition and breakage [10]. High-shear granulation is a complex process and the influence of various parameters has been studied [11–13]. An extensive review on wet granulation was given by Iveson [10].

To our knowledge, only one abstract is found in the scientific literature on the granulation of pillared clays [14]. Objectives of the present work were (a) preparation of GIOCs by high-shear wet granulation using different operating conditions, (b) the characterization of the materials: size distribution, morphology, disintegration test, friability, chemical structure and (c) the impact

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[*] Corresponding author. Tel.: +33 5 55 45 72 04/73 67; fax: +33 5 55 45 72 03.
E-mail address: michel.baudu@unilim.fr (M. Baudu).

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Table 1
Physical properties of mixed pillared clay.

Particle size analysis (μm)	
d_{10}	10.53
d_{50}	47.15
d_{90}	136.10
True density ρ_s (g/cm^3)	2.11
BET surface area (m^2/g)	13.26

Table 2
Kinetic constants from pseudo-first-order model.

	K_1 ($\times 10^{-2}$ min^{-1})	R^2
Powder	7.40 ± 0.11	0.998
300 μm < d_p < 400 μm	4.56 ± 0.35	0.989
400 μm < d_p < 600 μm	3.482 ± 0.30	0.985
700 μm < d_p < 800 μm	2.83 ± 0.20	0.979
1000 μm < d_p < 1200 μm	2.59 ± 0.20	0.983

of wet granulation on the kinetics constants and adsorption capacities of GIOCs. For this last objective, we used a basic dye (Basic Yellow 28, BY28) currently used in the Algeria's textile industry as model pollutant.

2. Materials and methods

2.1. Materials

Al-cetyltrimethylammonium bromide intercalated clay (CTAB-Al-Mont Na) (Table 1) was synthesized from a West Algerian bentonite (Maghnia deposit) supplied by Entreprise Nationale des Substances Utiles et des Produits Non-Ferreux (ENOF, Algeria) according to previous reported methods [7,15]. The intercalation of montmorillonite by the pillaring solutions was obtained with the following parameters: final concentration $[\mathrm{Al}]_f = 0.1$ M, molar ratio OH/Al = 1,8, Al/montm-Na ratio = 4 mmol/g.

After vacuum filtration and several washing with Milli-Q water, the solid product obtained was dried at 40 °C to a constant weight for at least 72 h, ground for homogenisation and sheltered from light. The surfactant-treated aluminium-intercalated clay was prepared by adding under mechanical stirring known quantity of surfactant (CTAB at concentration of 2 g/L) to a dispersion of aluminium-pillared montmorillonite (0.5%). The surfactant/clay ratio was fixed at (5 mmol/g) of surfactant per gram of clay.

Final solid products were separated by vacuum filtration. The excess of physically adsorbed alkyl ammonium cations and of physically bonded cations were removed by several washing.

Binder solution was a hydrophilic silicone-acrylic polymer (industrial grade) supplied by LION (Italy).

Basic Yellow 28 was purchased from FLUKA. Stock aqueous solution (1 g/L) was prepared in Milli-Q Water and experimental solutions were obtained by successive dilutions.

2.2. Experimental set-up and granulation procedure

GIOCs were produced in a small-scale laboratory high-shear mixer (Fig. 1a). This mixer includes a vertical stainless steel bowl (internal diameter: 80 mm; volume < 150 mL) with two agitators: the first one is a flat three-blade impeller symmetric to the bottom

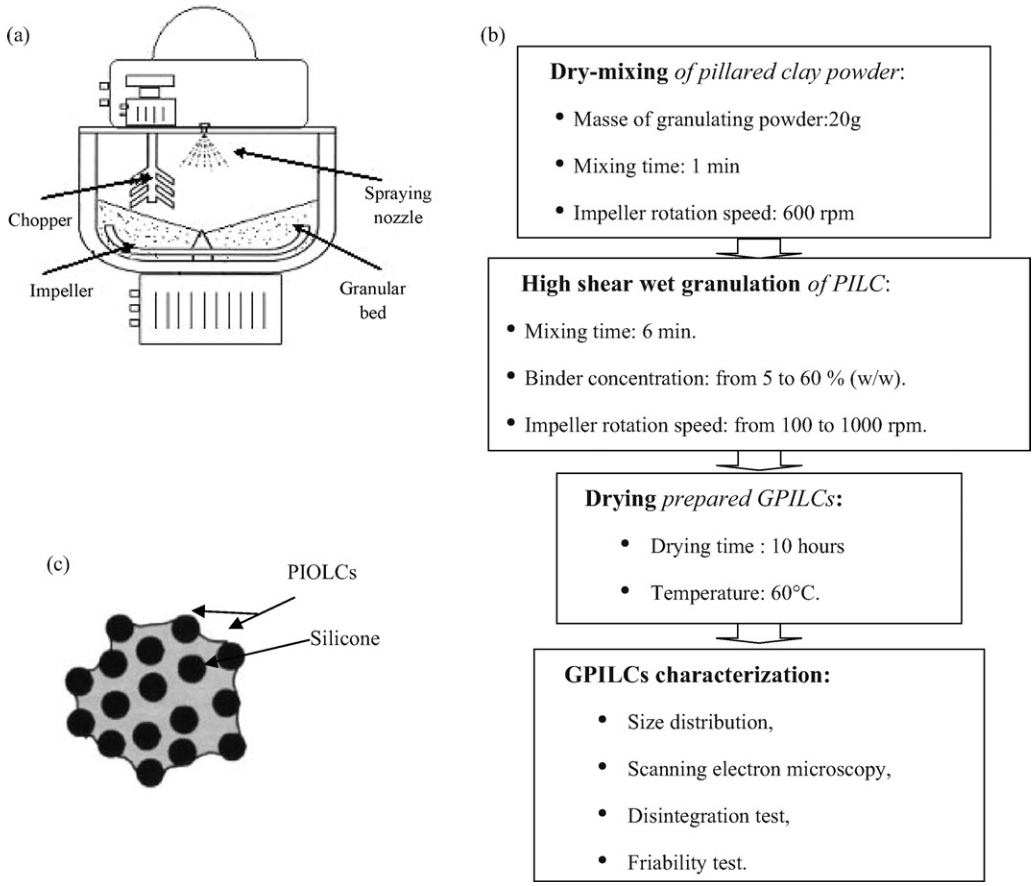

Fig. 1. (a) Experimental set-up and (b) granulation procedure and (c) schematic representation of the GIOCs from [16].

of bowl and the second one is a chopper blade at the top of the bowl. The rotational speed can vary from 0 to 1000 rpm. Since the chopper did not influence the granulation process, it was not used in this study. Binder droplets were sprayed on PIOCs powder in rotation using a manual spraying system at different times. Operating procedures are summarized in Fig. 1b.

Twenty grams of PIOCs was introduced into the mixer and homogenised by dry-mixing for 1 min with an impeller rotation speed of 600 rpm. This step was followed by the wet granulation procedure which consisted of spraying binder solution at different concentrations (5–60%, w/w, in Milli-Q Water), onto the powder bed. The impeller was started concurrently, and the powder bed was mixed for 6 min. The operation time was taken from the start of binder addition. After granulation, the solids were collected and spread out on a tray for drying in a shelf drier. The temperature of 60 °C was chosen to allow the evaporation of the wetting agent (water) without altering the characteristics of the binder agent (silicon). Based on previous work [16], GIOCs in this study are structured aggregates of PIOCs.

2.3. Characterization

In order to evaluate the effect of binder concentration on wettability, a capsule of pillared clay powder with a diameter of 10 mm and a length of 12 mm was manufactured using a Carver Press (Carver Press Inc., Model C) at a pressure of 10 000 psi. A drop of binder solution with a volume of 4 µl was added to the compact powder and observed by a video camera (CCD THOMSON CSF). The contact angle between the powder and the binder was performed by image analysis using the Young–Laplace equation [17].

The dynamic viscosity was measured by an automated dynamic shear rheometer (Rheometer Rheolab MC1 US 200 Physica, Germany) at 25 ± 1 °C.

The disintegration tests were carried out at 25 °C during 24 h in a mechanical shaker containing 800 mL of distilled water and a stirrer speed of 200 rpm. No sample (6 granules) disintegration by the end of the test indicates the solids to be resistant.

The friability tests were performed using a Roche friabilator (ERWEKA TA3R, Germany). A sample of twenty granules was initially weighted (m_1) and run in a drum for 10 min at 25 rpm. Granules were weighted ($\mathrm{m_2}$) and friability (%) was calculated according to Eq. (1):

$$F\ (\%) = \left(\frac{m_1 - m_2}{m_1}\right) \times 100 \tag{1}$$

Dry-sieving was performed using sieves (100–1500 µm) on a vibrating sieve-shaker (RETSCH AS 200; Germany) for 10 min with an amplitude of 2 mm and a frequency of 50 Hz.

Infrared spectra were obtained using a Fourier transform infrared spectrometer (Perkin-Elmer 1720 FTIR). The XRD pattern was recorded using a XRD SIEMENS D5000 from 2 to 30° with a scanning speed of 0.03° of 2θ per second (Cu Kα radiation, 1.5406 Å). Solid morphology was determined by scanning electron microscopy (PHILIPS XL30 with EDS and an EPMA CAMERA SX 100).

2.4. Adsorption of Basic Yellow 28

Kinetic experiments were conducted in brown flasks at room temperature by shaking 0.1 g of adsorbent (PIOCs and GIOCs) with 100 mL of the dye solution (100 mg/L) at 200 rpm on a mechanical shaker (IKALABORTECHNIK MODEL KS 501). The samples were withdrawn at intervals from 10 to 480 min and analyzed by spectrophotometry at $\lambda_{\max} = 455$ nm.

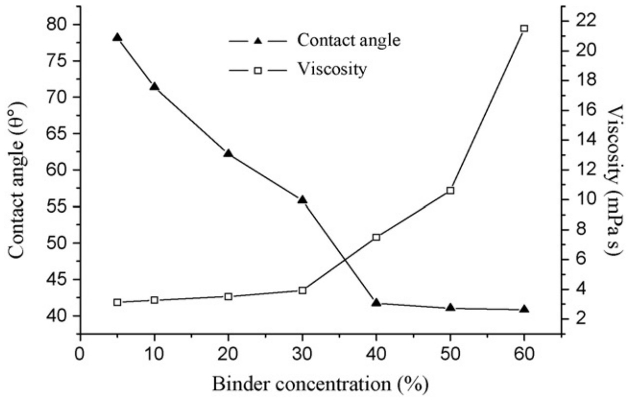

Fig. 2. Contact angle and dynamic viscosity variations with binder concentration.

Isotherms studies were conducted by shaking different quantities of sorbent (from 0.01 to 0.1 g) with 100 mL of the dye solution (100 mg/L) at pH 3 and 6.

3. Results and discussion

3.1. Granulation parameters

Dynamic viscosity versus binder concentration is plotted in Fig. 2. Between 5 and 30%, viscosity slightly increases followed by an important rise at higher concentrations. In contrast, the contact angle (Fig. 2) decreased leading to a better wetting of the hydrophobic surface of PIOCs. Contact angle remains constant for binder concentrations higher than 40%.

Binder content is one of the main parameters affecting the growth of granules; experiments were conducted by varying the binder to solid ratio from 5 to 100% (w/w) with constant binder concentration (40%) and impeller rotational speed (600 rpm). Three growth stages were obtained (Fig. 3). For low binder content ($H < 20\%$), the proportion of fine particles were not modified, this stage corresponds to the wetting and nucleation regime. Stage 2, characterized by a sudden decrease of fine particle ($d_p << 300$ µm) and the apparition of intermediate size granules (300–800 µm) occurs for liquid to solid ratios between 20 and 80%. Finally, an uncontrolled growth stage takes place for content up to 80%. Liquid to solid ratio was fixed to 80% in this work.

Mechanical resistance increased with binder concentration and a maximum was attained for 40% (Fig. 4a). An explanation was the improved force of the dried bridge which binds the primary particles of PIOCs. Size distribution is scarcely modified by binder concentration (Fig. 4b). For low binder concentrations (i.e. large contact angle), PIOCs particles will have a smaller area covered by the liquid binder in the mixer and therefore a low probability to hit another wet particle during random collision whereas low contact angles (high concentration) imply the particles to be wet by binder liquid and to increase the growth of the agglomerate.

At low-shear granulation (from 100 to 400 rpm), the impeller helped the formation of fine particles. But above 600 rpm, larger particles were formed due to intense agitation, which leads to a good dispersion of binder on the powder bed. This is in accordance with previous results [18,19].

Furthermore, the friability results for a binder concentration of 40% (Fig. 5a) indicate that the increase in the shear reduces the friability from 5.75 to 0.5% confirming that the high impeller speed induces good mixing between the liquid binder and the PIOCs powder leading to formation of high hard

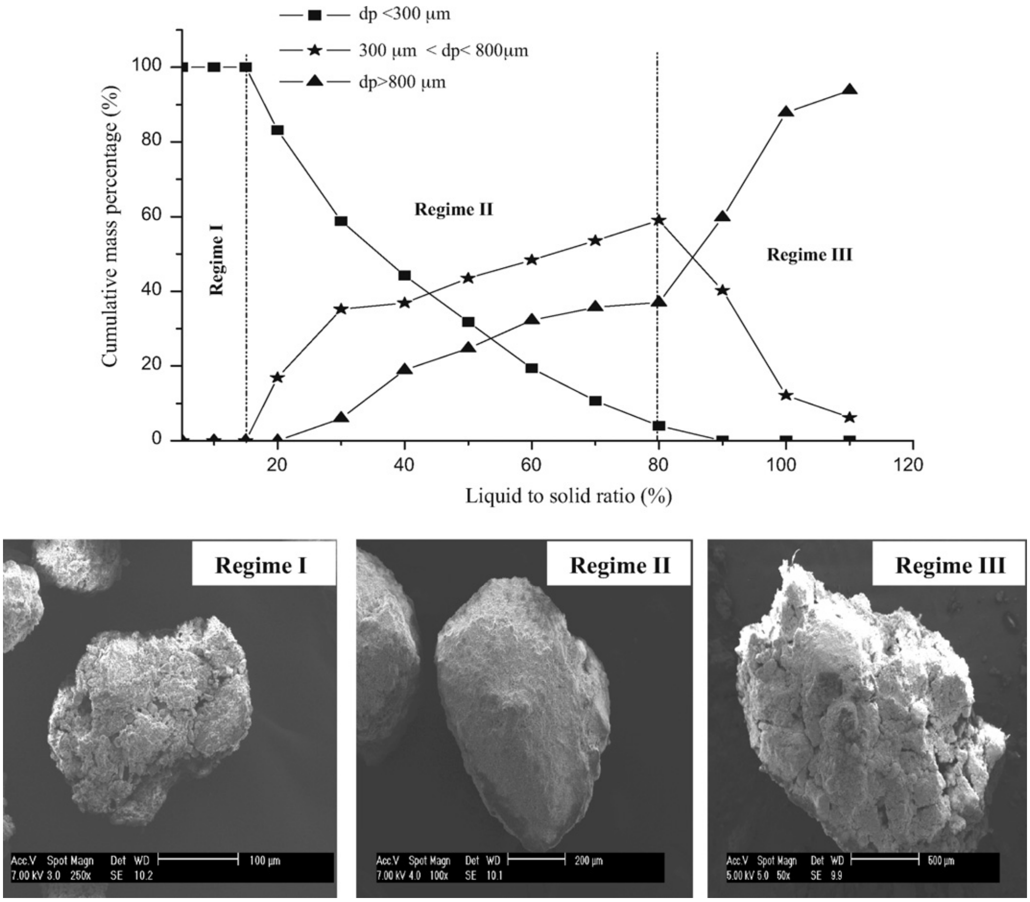

Fig. 3. Size fractions variations versus liquid to solid ratio.

granules. In addition, disintegration tests reveal that granules are resistant to water for impeller speed equal or higher to 200 rpm. On the other hand the sphericity increased with impeller speed.

3.2. Physico-chemical characterization

The FTIR spectra of PIOCs, silicone binder and GIOCs are given in Fig. 6. No chemical reaction occurs between the starting materials. GIOCs exhibit four main peaks. The band near 3626 cm^{-1} has been assigned to the stretching (γ-OH) vibration of OH groups attached either to aluminium or magnesium. The intense band appearing around 2920 and 2850 cm^{-1} can be attributed to asymmetric and symmetric CH stretching vibrations of $-CH_2$ groups in the quaternary ammonium molecules between the silica layers. Band around 1640 cm^{-1} is due to the OH deformation of water and the peak at 1035 cm^{-1} was attributed to the asymmetric stretching vibration of SiO_2 tetrahedra.

XRD patterns of GIOCs shows that, the interlamellar spacing (d_{001}) after granulation remains constant (18.4 Å) indicating that the binder (silicone) does not penetrate the interlayer regions of PIOCs.

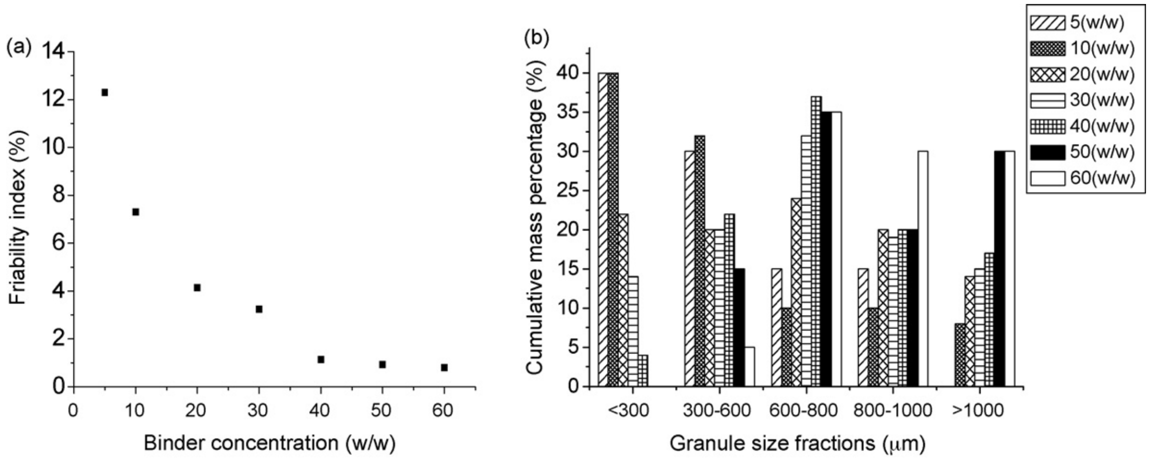

Fig. 4. Influence of binder concentration on: (a) GIOCs friability index and (b) cumulative size fractions of GIOCs.

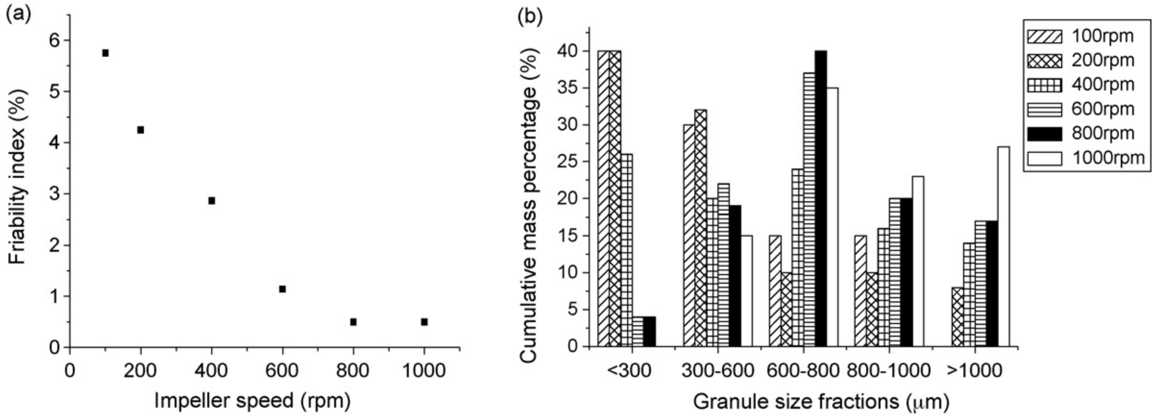

Fig. 5. Influence of impeller speed on: (a) GIOCs friability index and (b) cumulative size fractions of GIOCs.

3.3. Adsorption of BY28 by GPILCs

Four GIOCs sizes were analyzed (300–400, 400–600, 700–800 and 1000–1200 μm); results were compared to starting material PIOCs powder (CTAB-Al-Mont Na, with $d_p < 50$ μm).

3.3.1. Kinetics

Starting material and the smallest sizes reached equilibrium within the first 60 min whereas the larger sizes took about 120 min. This may be due to the large surface area of the smallest particles (Fig. 7) and a lower driving force area for mass transfer [20–22]. Similar size effects were reported for the adsorption of dyes on granular activated carbon [23,24].

The rate constant of BY 28 adsorption was determined using the Lagergren's pseudo-first-order model [25] using the following equation:

$$q = q_e(1 - e^{k_1 t}) \tag{2}$$

where q_e and q (mg/g) are respectively the amounts of dye adsorbed at equilibrium and at any time t (min) and k_1 (min^{-1}) is the rate constant of pseudo-first-order model adsorption.

Fitting of the experimental results were done by non-linear regression (Table 2). The pseudo-first-order model properly depicts the adsorption process in agreement with the results of Yener [26] for the removal of Basic Yellow 28 by amberlite. The powder had a significantly higher rate constant ($k_1 = 7.40 \times 10^{-2}$ min^{-1}) than granular forms and rate constants decreased with size which indicates that the sorption rate is affected by mass transfer. Ho's pseudo-second-order model [27] failed to improve the sorption results.

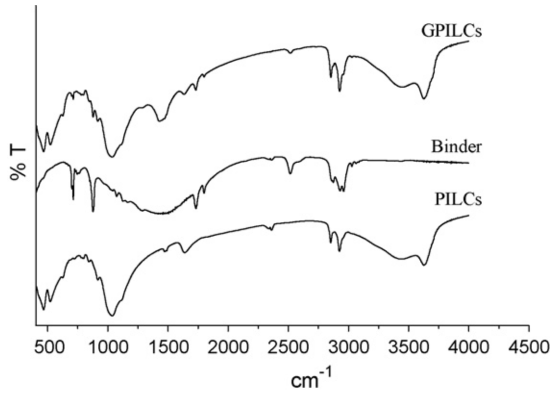

Fig. 6. FTIR spectra of PIOC, silicone binder and GIOC.

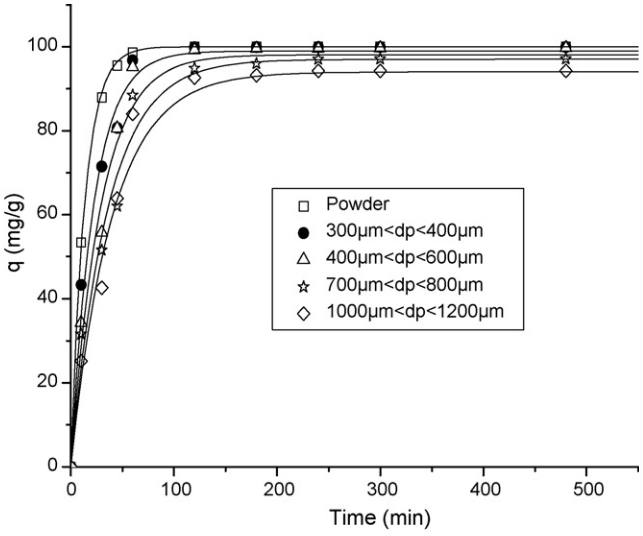

Fig. 7. BY 28 adsorption kinetics.

Rate constants k_1 (min^{-1}) versus the inverse of particle size ($1/d_p$) was plot in Fig. 8. Adsorption kinetic follows a surface diffusion law:

$$k_1 = 0.014 + 10.31\left(\frac{1}{d_p}\right) \tag{3}$$

with coefficients of determination (R^2) of 0.984.

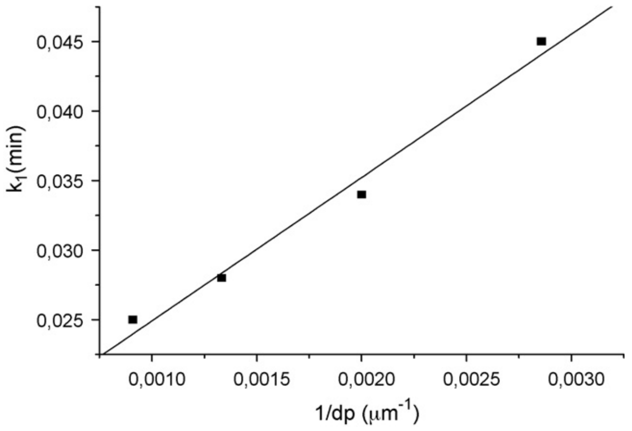

Fig. 8. Rate constants versus inverse of the particle sizes ($1/d_p$).

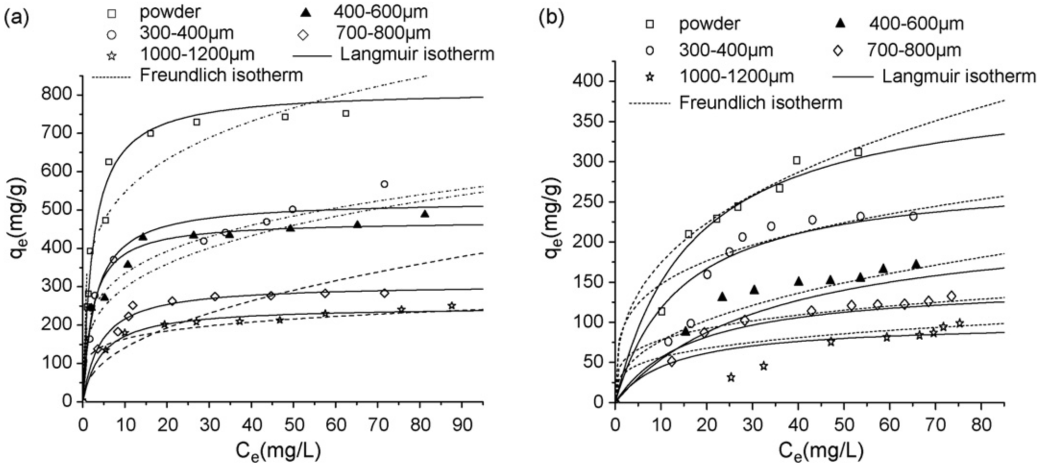

Fig. 9. Adsorption isotherm for BY28 removal by PIOC and GIOCs: (a) pH 6 and (b) pH 3.

Table 3
Adsorption isotherm constants for adsorption of BY28 on different classes of pillared clays.

	pH	Langmuir		
		Q_{max} (mg/g)	K_L (mg^{1-n} L^{3n}/g)	R^2
Powder	3	408	0,06	0.990
	6	780	0.45	0.980
300 µm < d_p < 400 µm	3	292	0.07	0.980
	6	514	0.35	0.958
400 µm < d_p < 600 µm	3	234	0.03	0.935
	6	464	0,44	0.807
700 µm < d_p < 800 µm	3	154	0.06	0.990
	6	307	0.23	0.980
1000 µm < d_p < 1200 µm	3	100	0.08	0.718
	6	247	0.22	0.932

3.3.2. Adsorption capacities

Adsorption isotherms for pH 3 and 6 are given in Fig. 9. The pH affects the sorbent charge surface and the ionization degree of sorbates [28]; dye removal increased from pH 3 to 6. At pH 6 > (pH_{PZC} = 5.3), the sorbent surface becomes negatively charged, thereby increasing electrostatic attractions between positively charged dye cations and negatively charge surface of adsorbent causing an increase in the dye adsorption. With the pH decrease (pH = 3 < pH_{PZC}), the adsorbent surface appears positively charged and sorption was unfavourable, probably because of excess H^+ ions and the electrostatic repulsion between the positively charged surface of adsorbent and the cationic dye molecules. A similar trend was also observed for the adsorption of Basic Yellow 28 by different adsorbents [28–30].

Binder adsorption capacity was determined (6 mg/g with concentration binder of 93 mg/L) and was not mentioned in Fig. 9.

Adsorption isotherms were analyzed by the Langmuir (Eq. (4)) and Freundlich models (Eq. (5)) using non-linear regression technique:

$$q_e = q_m \frac{k_L C_e}{1 + k_L C_e} \tag{4}$$

$$q_e = K_F C_e^n \tag{5}$$

where q_e (mg g^{-1})and C_e (mg/L), are respectively, the dye concentration adsorbed and in solution, q_{max} (mg/g), K_L (mg^{-1}) are the Langmuir constants related to the sorption capacity and energy, respectively, K_F is the Freundlich constant (mg^{1-n} L^{3n}/g).

A theoretical plot of the Langmuir and Freundlich isotherm models fitted with the experimental data is shown in Fig. 9. It illustrated that adsorption of BY28 onto PIOCs and GIOCs obeyed the Langmuir isotherm model as well. Values of the Langmuir constants (Q_{max}, K_L and correlation coefficients (R^2)) given in Table 3, indicates the monolayer coverage of dye.

The maximal adsorption capacity onto GIOCs were recalculated and expressed per mass unit of active adsorbent i.e. pillared clay (Q^*_{max}). Fig. 10 shows the corrected adsorption capacities of various classes of pillared clay for the BY28 at pH 6. The comparisons of the Q_{max} value of raw pillared clay (780 mg/g) and corrected Q_{max} for both classes show that the active mass of pillared clay is reduced by the binder. The adsorbent surface is limited by the attendance of

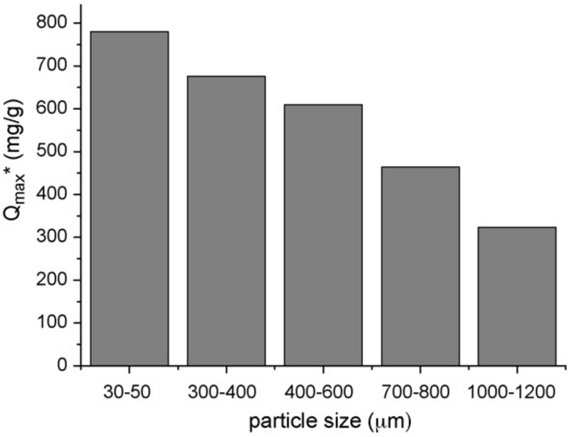

Fig. 10. Adsorption capacities of GIOCs (pH 6).

Table 4
The maximum adsorption capacity (mg/g), Q_{max}, of Basic Yellow 28 for various adsorbents.

Adsorbent	Q_{max} (mg/g)	pH	Reference
Clinoptililite	59	6–6.5	[26]
Boron industry waste	75	9	[28]
Bentonite	256	8	[29]
Green alga	27	8	[31]
Activated carbon (F-400)	860	–	[32]
Activated carbon (palm-fruit bunch)	600	–	[32]
PILCs	780	6	(This study)
GPIOCs			
300 μm < d_p < 400 μm	514	6	(This study)
400 μm < d_p < 600 μm	464	6	(This study)
700 μm < d_p < 800 μm	307	6	(This study)
1000 μm < d_p < 1200 μm	247	6	(This study)

silicone and the adsorption capacity is weakly reduce for the lowest granule size (13%) but greatly for the largest size (48%).

The favourable nature of adsorption can be expressed in terms of a dimensionless constant called as separation factor or equilibrium parameters R_L, which is defined by Namasivayam and Ranganthan [32], as

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of dye. The K_L was found in all cases between 0 and 1 indicating favourable interactions between BY 28 and adsorbents.

The maximum sorption values (Q_{max} (mg/g)) in the present study were compared with other adsorbents (Table 4). It can see that GIOCs, show great potential as an adsorbent for Basic Yellow 28 close to the capacity of activated carbon.

4. Conclusions

The purpose of the current work was to prepare coherent and consistent pillared clay granules intended for the treatment of polluted waters by the adsorption process using a small-scale laboratory high-shear mixer granulator. Experimental data showed that for a fixed values of binder amount, the binder concentration and impeller speed have a significant effect on the size, friability and disintegration of obtained granules. An increase in each of those parameters can result in the formation of granules with very different characteristics. Based on these results, the experimental conditions of pillared clay wet granulation are 80% (w/w) liquid to solid ratio, 40% (w/w) binder concentration and an impeller speed of 800 rpm.

The impact of wet granulation on the kinetics and adsorption capacities of GIOCs was estimated using Basic Yellow 28 model pollutant. Kinetic studies reveals that BY 28 adsorbed faster in powder pillared clay ($k_1 = 7.40 \times 10^{-2}\ \text{min}^{-1}$) than in granular ones. The results best fitted the pseudo-first-order kinetic model. The adsorption equilibrium data were analyzed by the Langmuir and Freundlich models using non-linear regression technique. The best fit to the data was obtained with the Langmuir isotherm. Moreover, when compared to powder pillared clay, the new generation of granules presented larger adsorption capacities (Q_{max} >300 mg/g at pH of 6) for the treatment of dyes from industrial wastewater.

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