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FORMULATION OF COMPOSITE BEADS ALGINATE/HYDROXIDE SLUDGE FOR THE REMOVAL OF DYES FROM AQUEOUS SOLUTIONS

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Abstract

To produce drinking water, the water treatment plants generate huge quantities of sludge, this sludge is a waste and they are evacuated to the dump. The valuation of these sludge will be benific This study focuses on the development of composite alginates beads and sludge activated chemically by sulphuric acid and thermally for the removal of dyes from aqueous solutions. Two dyes were studied; a basic cationic dye (methylene blue) and an acidic anionic dye (Congo red) to compare the adsorption mechanisms of the two dyes. This study proposes a combination of the adsorbent potency of alginates and water treatment sludge. The alginates /sludge ratio was studied to determine the best formulation. Subsequently the effect of the crosslinking agent, drying, thermal and chemical activation, contact time, mass of the composite beads and the effect of pH on the yield discoloration was studied. The results of adsorption kinetics of MB (methylene blue) and CR (Congo red) are better described by the pseudo second-order model. The adsorption isotherms of the two dyes are satisfactorily described by the Langmuir model. Activation of the sludge makes it possible to improve the adsorbent capacity of the beads.

Key words: activation, bead, drinking water, dye, sludge

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1. Introduction

Sludge is the residue from water treatment processes, it is a waste for treatment plants, several authors have worked on their recovery in the treatment of water (Babatunde et al., 2010; Li et al., 2011; Pilli et al., 2011; Scalize et al., 2018; Yang et al., 2014).

Nair and Ahammed (2015) found that the use of aluminum from sludge with polyaluminium chloride pretreatment for the post-treatment of UASB (upflow anaerobic sludge blanket) reactor treating urban wastewater with a dose of 15g/L allows the elimination of 74% of COD (Chemical Oxygen Demand), 89% ofturbidity, 79% of phosphorus, 84% of suspended solids, 78% of BOD (Biological Oxygen Demand) and 99.7% of total coliforms. Jangkorn et al. (2011) found that sludge aluminum alone could significantly eliminate turbidity and COD. Chu (2001) studied the removal of dyes from a textile release by coagulation by recycled aluminum sludge and reported an elimination efficiency of 88% of hydrophobic dyes, however, the method is not effective for hydrophilic dyes. Other researchers have worked on the valorization of sludge as an adsorbent for the treatment of metallic pollution such as Cu (II), Pb (II), Cr (III) and Hg (II) (Lin et al., 2014; Predescu et al., 2017).

Water treatment sludge was used for the removal of dyes. Rashed et al. (2016) found that a sludge mass of 0.25g/100ml activated at a temperature of 700°C gives good MB decolorization efficiency. Yusuff et al. (2017) studied modeling of adsorption of MB dye on sludge by experimental design. They found a 100% bleaching efficiency at pH 6, an

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adsorbent concentration of 1.55g/L, an initial concentration of 159 mg/L of MB and a contact time of 120min.

Sludge is a good adsorbent but some problems arise during the implementation of the adsorption such as the difficulty of separation. Encapsulation is a process that solves this problem. It is an economic and ecological technique to immobilize a material in a hydrogel matrix while maintaining their adsorbent properties.

Alginate is one of the most used polymers to remove pollutants in solution. They are very abundant polysaccharides in nature, and they have been widely used as adsorbents in aqueous solutions because of their low cost of preparation, their biodegradability and the absence of toxicity (Errais et al., 2012; Zhao, 2016).

In addition to its adsorption capacity, alginate is characterized by the property of forming gels in the presence of divalent cations, such as calcium and barium ions. These properties allow the combination of adsorbent by encapsulation and the development of materials that can be implemented in water treatment processes. The formed beads can be used after and saturation can be recovered by a simple separation.

Several authors have used alginate beads for the treatment of pollutants (Njimou et al., 2016; Sujitha and Ravindhranat, 2017); others have used alginate composite material beads with adsorbents such as raw drinking water sludge (Poormand et al., 2017); Double Lamellar Hydroxydes (Phuong, 2014; Zhao, 2016); iron nanoparticles (Lee et al., 2016); zirconium (Prabhu and Meenakshi, 2015); nano-hydroxyapatites (Pandi and Viswanathan, 2015; Sarker et al., 2015), aluminum (III) particles (Zhou et al., 2014); volcanic composites (Chen et al., 2014); and grape waste (Lezehari et al., 2012).

Alginates have also been used to encapsulate biological cells for the treatment of pollutants such as phenoland hexavalent chromium (Humphries et al., 2005). Martinez et al., (2009) studied the encapsulation of micro-organisms contained in activated sludge with calcium alginates in a tubular reactor for the treatment of wastewater.

This study focuses on the preparation of sodium alginate beads encapsulating water treatment sludge chemically and thermally activated. The absorbent properties of this composite material were evaluated using cationic dye MB and anionic dye CR. The composite sludge/ alginate beads make it possible to combine the properties of the encapsulated adsorbent (raw sludge and activated sludge) as well as those of the alginate gel.

2. Materials and method

2.1. Sample collection

The sludge samples are taken directly from the decanters of the drinking water treatment plant of the Bin el Ouidane Dam (Beni Mellal region). The liquid sludge is decanted and dried and then placed in an oven at a temperature of 105 °C.

2.2. Acid activation

The sludge is activated by a sulphuric acid solution at concentrations of 0.5M, 1M, 2M and 5M at a temperature of 25°C, in the proportions of 10 g of sludge per 100 mL of solution for 3 hours. The sludge /acid mixture is then separated by centrifugation. The solid phase is washed several times with hot double distilled water to remove the excess sulphuric acid impregnating its external surface, dried in an oven at 80 °C for 48 hours, milled and then stored away from moisture up to the moment of use.

2.3. Thermal activation

The dried sludge is placed in the oven at temperatures of 350°C, 500°C, 700°C, 800°C, 900°C and 1000°C.

2.4. Synthesis of composite beads

The raw sludge (RS) is washed with distilled water to remove impurities and then dried in an oven at a temperature of 105°C for 24h, the sludge is then ground and sieved to obtain fractions <80 microns.

A mass of RS is stirred in 100 mL of distilled water until the solution becomes homogeneous and a mass of 1g of sodium alginate is added slowly, the solution is stirred for 2 hours until obtaining a homogeneous gel. The alginate/sludge mixture is introduced into a solution of calcium chloride $CaCl_2$ at 0.1 mol/L bymagnetic stirring. The mixture (Sludge, Alginate beads and calcium chloride solution) is allowed to stand for a maturation time of 10 hours. Then the beads are filtered and washed several times with distilled water to remove free calcium ions. The wet beads are kept in distilled water and others are put in an oven at a temperature of 60°C to dry.

The characterization of the sludge alginate composite material is carried out by DRX and IR. The experiments were carried out by introducing different masses of alginate beads/sludge into the 20mg/L concentration solutions of the cationic MB dye or the anionic CR dye. The solid liquid separation is carried out by centrifugation at 5000 rpm for 5 minutes in order to avoid any adsorption on filter paper. The supernatant obtained was analyzed by UV-visible spectrophotometry at a wavelength λmax = 661 nm for the MB and at λmax = 498.5 nm for the CR.

The adsorbed amount is calculated using Eq. (1):

$$Qads = (C0 - Ct) \cdot {}^{V}\!/_{M} \qquad (1)$$

where: Qads: amount adsorbed at time t in (mg/g); V: volume of the solution in (ml); C_0 and C_t: are, respectively, the initial concentration and the concentration at time t of the dye in (mg /L); M: mass of the adsorbent in (g).

2.5. Dye solution

Methylene blue (MB), cationic dye (basic) belonging to the class of Xanthines, chemical formula $C_{16}H_{18}N_3SCl$, molar mass 319.86 g/mol, its wavelength maximum absorption $\lambda max = 661nm$, initial pH of MB solution is 8.2.

Congo red (CR), anionic dye (acid) belonging to the class of azo, of chemical formula $C_{32}H_{22}N_6O_6S_2Na_2$, molar mass 696.7g/mol, its maximum wavelength Absorption $\lambda max = 498.5nm$, initial pH of the solution of the Congo red is 5.43.

3. Results and discussion

3.1. Characterization of composite beads alginate / hydroxide sludge by XRD and IR

The mineralogical composition of the beads was determined by X-ray diffraction on dried powder of the crushed composite beads. The analysis of the diffractograms (Fig. 1a) allows us to note a strong presence of free silica in the form of quartz identified by its characteristic line (2θ=26.75°). The calcite was identified at (2θ = 29.60°) and the alginate at (2θ=31.76°). The composite alginate and sludge beads activated with 2M sulfuric acid contain sulphates identified by a peak at (2θ=28.32°) and kaolinite is identified by its characteristic line (2θ=25.58°).

According to the infrared spectrum (Fig. 1b), the following main peaks can be assigned for the three formulations:

- a band at 499 cm^{-1} characterizes the Si-O-Al binding vibration.
- a band at 530.7 cm^{-1} characterizes the Si-O-Al bonding vibration
- a band at 910 cm^{-1} characterizes the Al-O-H bonding vibration
- bands at 798.4 - 694.5 and at 1030 cm^{-1} characteristic of the quartz Si-O bond, these bands are wider for the composite alginate/sludge beads at 350°C and the sludges activated with 2M of sulfuric acid.
- an intense wide band characterizes the alginate vibration at 1634 and 1544 cm^{-1} due to carboxyl anions.
- a characteristic band of C-O-C bonds at 1037 cm^{-1}.
- a band at 3650 cm^{-1} characteristic of the O-H bonds disappears for the composite beads of activated sludge at 350°C.

3.2. Removal of dyes from aqueous solutions with composite beads alginate/hydroxide sludge

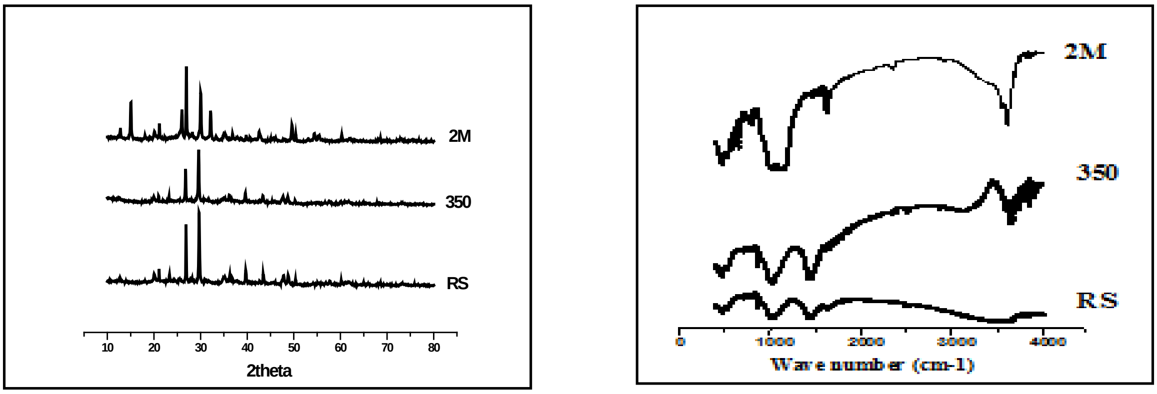
3.2.1. Effect of formulation of beads on the adsorption of MB and CR

In order to determine the quantity of sludge to be in contact with the alginates, several formulations were developed, masses of sludge (from 0.5 to 6g) are stirred in 100 mL of water. After homogenization, 1g of powdered sodium alginate is slowly added to the suspension, which is kept under rapid stirring. The sludge-alginate mixture is then introduced into the crosslinking agent (calcium chloride). The measurements are carried out during 2 hours.

Fig. 2 shows that the adsorbent capacity of the mud-alginate composite material increases with the increase in the mass of the encapsulated sludge. At a mass greater than 5g of sludge the solution becomes very viscous and the formulation of beads becomes impossible. The best formulation is that composed of 1g of alginate and5g of sludge.

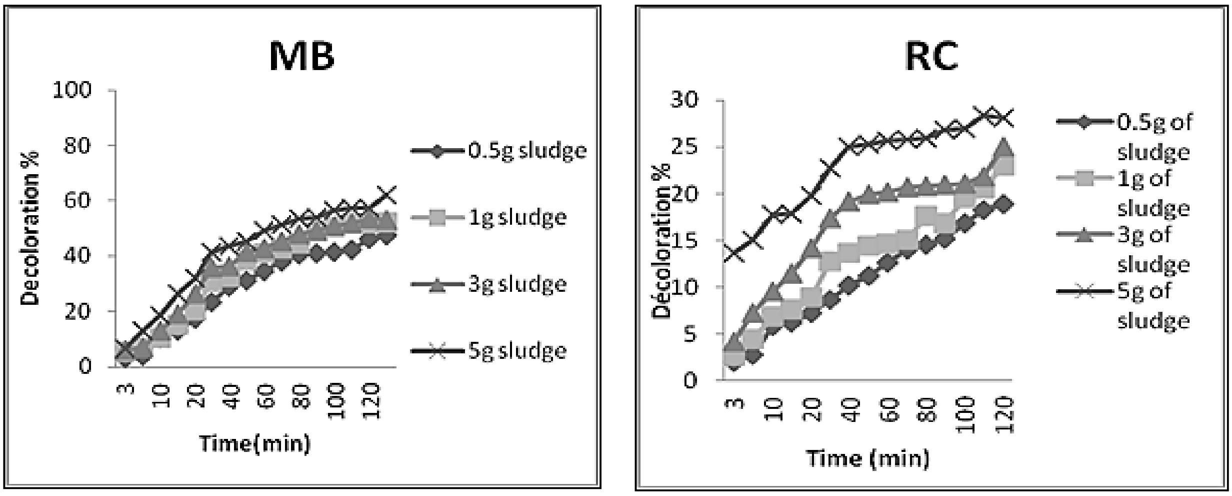
3.2.2. Effect of crosslinking of beads *on the adsorption of MB and CR*

The main characteristic of alginates is its gelation property with bivalent and trivalent cations. For the formulation of composite beads (alginates / raw and activated sludge), four crosslinkers was used, two bivalents ($Ca^{2+}$and Ba^{2+}) and two trivalents ($Al^{3+}$and Fe^{3+}). The crosslinking agent used does not influence the diameter, the moisture content or the density of the beads (Zhao, 2016).Fig. 3 shows that the adsorption kinetics of the calcium-crosslinked beads is faster compared with barium and the aluminum sulfate-crosslinked beads give the lowest yield compared to the others for the adsorption of the cationic dye. methylene blue. However the opposite effect was observed for the CR.



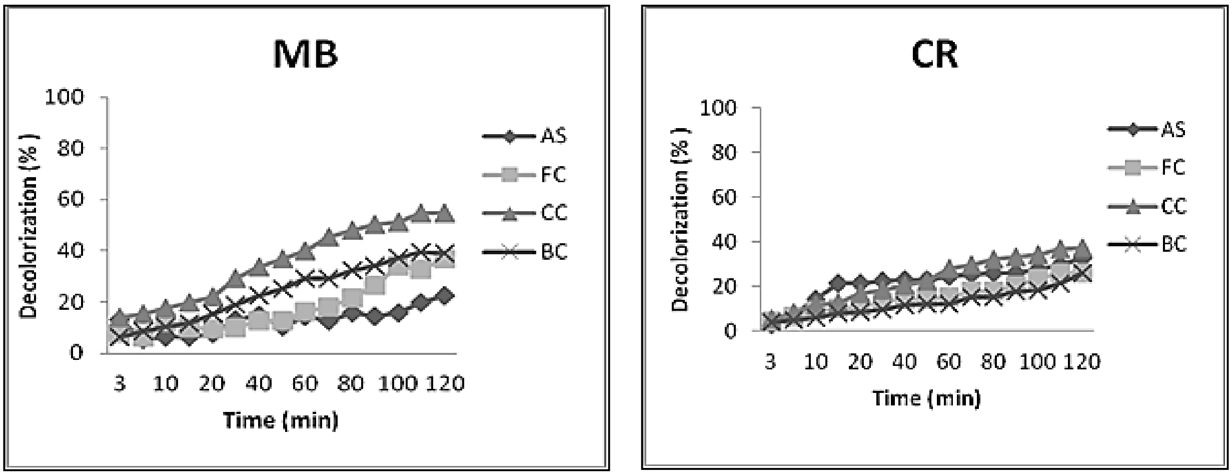
(a) (b)

Fig. 1. DRX (a) and Infra-red (b) spectra of composite alginate/raw sludgeand activated sludge beads



(a) (b)

Fig. 2. Effect of the formulation *of* beadsalginates / sludges on adsorption of MB and CR(Ci dyes = 20mg/L, adsorbent mass 5g/L (wet beads), ambient temperature,pHCR = 5.85, pHMB = 8.2, Time: 2h): (a) represent the adsorption of MB,(b) represent the adsorption of CR



(a) (b)

Fig. 3. Effect of crosslinking agent on the discoloration of MB and RC (Ci dyes =20mg/L,adsorbent mass 5g/L (wet beads), Ambient temperature, pHCR = 5.85, pHMB = 8.2, Time: 2h),CC: Calcium chloride, BC: Barium chloride, AS: Alumina sulphates, FC: Ferric Chloride, (a) represent the adsorption of MB, (b) represent the adsorption of CR

The beads crosslinked by ferric chloride are less dense and less consolidated, they disintegrate with agitation.The results show that the use of calcium as crosslinking gives good decolorization yield for the two anionic and cationic dyes (CR and MB). The crosslinking by Ba^{2+} ions makes it possible to obtain a greater rigidity of the alginate gel, but this structuring, which slightly improves the kinetics , reduces the mass of adsorbent accessible to the adsorbate with a very slow transport in the center of the ball (Bierhalz et al., 2014). However Bierhalz et al. (2014) and Mallepally et al. (2013) found good results with barium chloride.

3.2.3. Effect of sludge activation on the adsorption of MB and CR

To improve their adsorbing power sludge have undergone thermal and chemical treatmentAcidic activation of sludge is intended to decrease interfoliar distance, the structural cations of the sludge (Al^{3+}, Fe^{3+}) are replaced by H^+ protons to lead to an increase in the surface acidity of the clay structure (Gannouni and Bellagi, 2001; Numan and Charles, 1969; Ross, 1968; Taylor and Jenkins, 1988). The chemical activation of the beads is carried out using sulfuric acid at concentrations of (0.5M, 1M, 2M and 5M) at 25 ° C. Tavani and Volzone (1999) found that clays activated with sulfuric acid have a greater catalytic activity than those treated with nitric and hydrochloric acids. This greater activity was attributed to the remaining sulfuric acid adsorbed on the surface of the clay at the time of activation.

During the formulation of the alginates/chemically activated sludge composite beads, it is necessary to thoroughly wash the sludge of the sulfuric acid until the complete disappearance of the sulphate ions, sludge containing high amounts of acid does not take spherical form because the mixture of alginates/sludge remains heterogeneous.

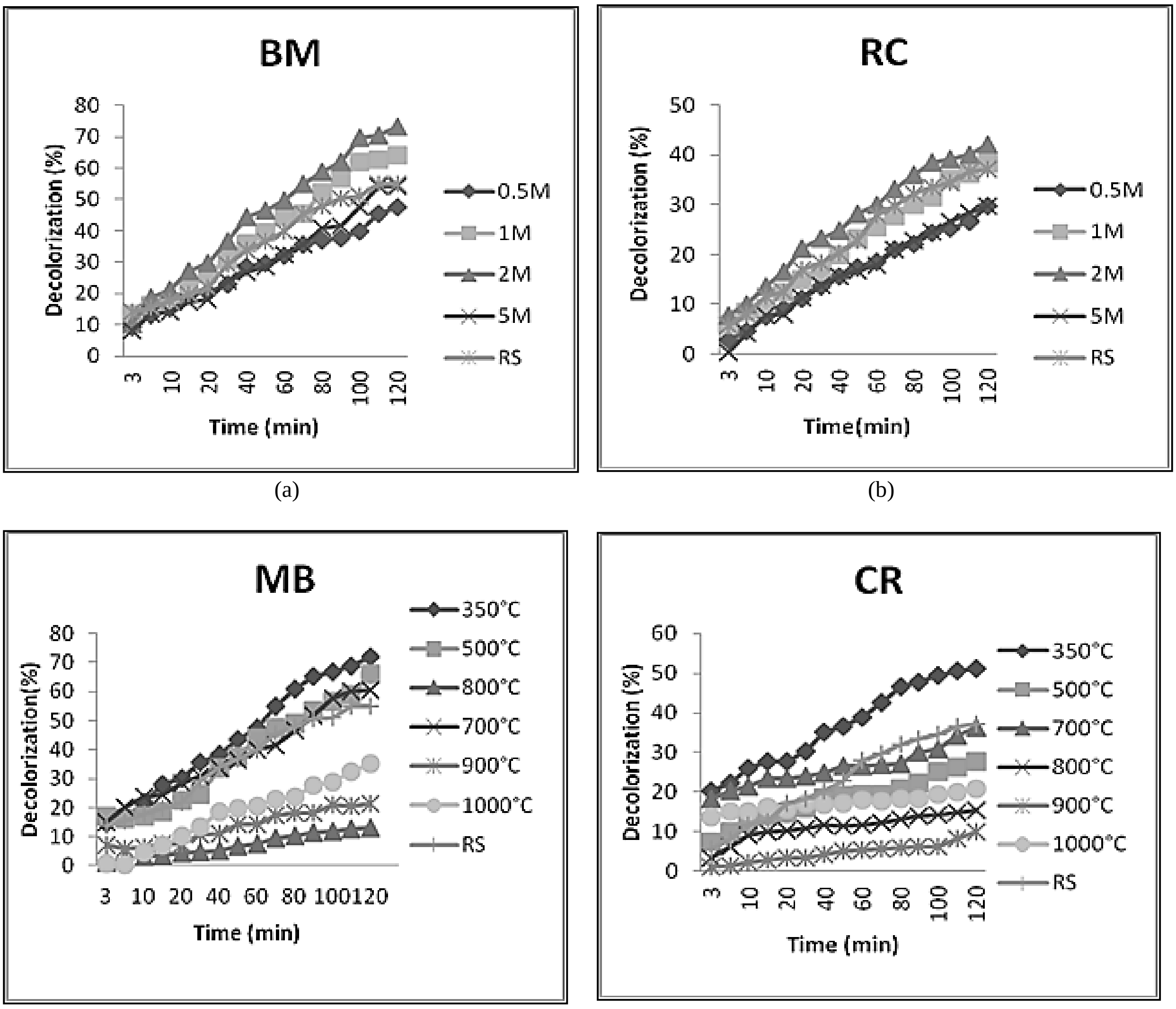
The results of the analysis (Fig. 4a-b) show that sludge purified with 2M sulfuric acid gives good discoloration for both dyes. This yield decreases for activated sludge with 5M sulfuric acid this can be explained by the collapse of the crystal lattice and the formation of amorphous silica during the attack with a high concentration of sulfuric acid (Neji et al., 2009).

To improve their adsorbent capacity the sludge have undergone by thermaltreatment at temperatures of 350, 500, 700, 800, 900 and 1000°C. The results of discoloration of MB and CR (Fig. 4c-d) show that the fading yield decreases with increasing temperature. The best yield is obtained by the composite beads of alginates and activated sludge at 350°C, this temperature allows the decomposition of the organic matter contained in the sludge and consequently the release of the adsorption sites on the adsorbent. This temperature is a characteristic of the dehydroxylation of kaolinite and the departure of structural OH (Rakotomaria et al., 2011).

3.2.4. Drying effect of composite beads *alginate / activated sludge on decolorization*

The drying facilitates the use of large-scale beads and their storage, for this purpose, the wet beads are subjected to drying in an oven at a temperature of 60°C for 24 hours. The size of the beads becomes smaller but they remain spherical. The analysis of results show that the discolouration efficiency increases with drying for raw and activated sludge formulations with 2M sulphuric acid and sludge activated at 350°C for BM. However the discoloration of CR is very low for RS and activated sludge with 2M sulfuric acid but there is a good discoloration yield for composite beads sludge at 350°C.

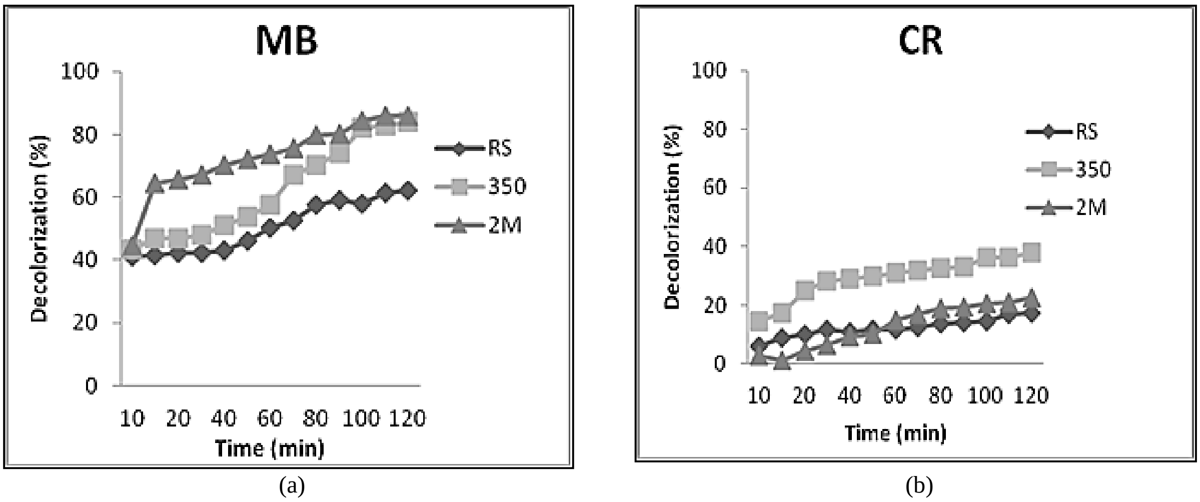
It is noted that the drying of the beads improves the discoloration yield (Fig. 5). However, several studies have shown that drying leads to the closing of pores and consequently the decrease of adsorption (Peric et al., 2008; Rocher, 2014).



(a) (b)

(c) (d)

Fig. 4. Effect of chemical (a-b) and thermal activation (c-d) on the decolorizationof MB and CR (Ci dyes = 20mg/L, adsorbent mass 5g/L (wet beads), Ambient temperature,pHCR = 5.85, pHMB = 8.2, Time: 2h)



(a) (b)

Fig. 5. Drying effect of composite beads on MB and RC decolorization (Ci = 20mg/L, adsorbent mass 5g/L, T = 29°C, pHRC = 5.85, pHMB = 8.2, Time: 2h): (a) represent the adsorption of MB, (b) represent the adsorption of CR

The results can be explained by the swelling in solution of these composite alginate/sludge beads which makes them looser and slightly more porous.

3.2.5. Kinetics of adsorption of MB and CR

100ml of dye at 20mg/L was put in contact with 5g of sludge to determine equilibrium time. The kinetics of adsorption of the two dyes (Fig. 6) is not very fast this may be due to the kinetic limitation on the diffusion of the dyes in the alginate gel. The fading efficiency increases with time up to 230 min this can be explained by the availability of free sites on the surface of the material and the strength of the interactions between the composite beads and the dyes. Subsequently the adsorption becomes slower and the adsorbed quantity is relatively low, this may be due to the molecular diffusion of the dyes to the less accessible adsorption sites because of their progressive saturation, the equilibrium time of the MB is 270min and for the CR the equilibrium time is 340min. This may be due to the availability of free sites on the surface of the material and the strength of interactions between sludge and dyes. Poormand et al. (2017) found that for a concentration of 50 mg/L of MB and a concentration of 0.3 g/L of composite alginates and RS the equilibrium time is 60 min. Rashed et al. (2016) found that a mass of 0.25 g/100 ml of raw and activated sludge, an initial MB concentration of 100 mg/L and a pH 7 the equilibrium time is 60 min. Zhao et al. (2016) found that the adsorbed amount increases over time for the ferrihydrite and HDL beads and that the pseudo-balance of phosphate adsorption is reached starting at 6 hours. Reddy et al. (2012) reported that the adsorption of CR on biomaterials requires a contact time of 3 to 7 hours. Li et al. (2015) found that the equilibrium time required for the adsorption of activated carbon dyes from urban sludge is 300 min for Acid Orange51 (anionic dye) and240 min for Safranine (cationic dye). Chiou and Li (2002) found that the adsorption equilibrium of RR 189 dye on chitozane beads was reached after 8 hours of shaking.

It is noted that the adsorption equilibrium time is shorter for the MB compared to the CR, this can be attributed to the characteristics of the dyes, the molecular mass and the size of the MB are smaller than those of the CR, which facilitates the diffusion of the dye molecules in the composite sludge beads. These results are in agreement with the results of the adsorption kinetics of Safranine and the acid orange on sludge from activated wastewater (Li et al., 2015).

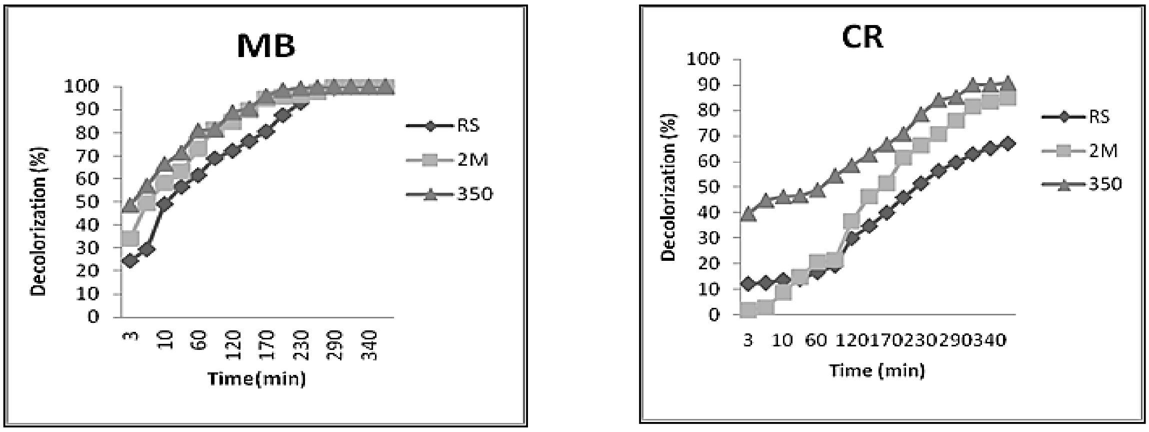
3.2.6. Mass effect of composite beads on discoloration

To study the mechanisms involved in MB adsorption by beads, The effect of the quantity of dry beads on adsorption was studied. Fig. 7 shows that the fading yield increases with the increase in the bead mass. The adsorption achieves a 95% discoloration efficiency at a mass of 15g/L of dry beads for MB and a 50% yield for CR for the beads with activated sludge at 350°C. The increase in discoloration yield with the adsorbent mass is explained by the increase of the adsorption sites on the beads. Rashed et al. (2016) found that the optimal sludge mass for MB decolorization is 0.25g/100mL. This difference in optimal masses can be explained by the difficulty of diffusion of MB in the alginate gel with respect to the activated sludge powder and also by the difference in specific surface area between the sludge powder and the sludge encapsulated in the alginates.

3.2.7. pH effect on discoloration of MB and CR

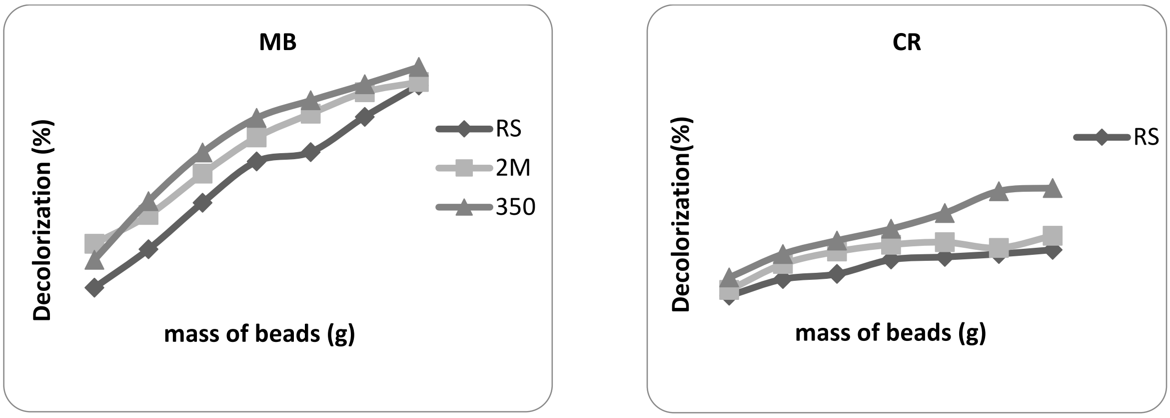
pH is a very important factor in adsorption, it can influence the available binding sites. The effect of pH on adsorption on composite alginate beads and hydroxide sludge was studied by varying the pH of the CR and MB dye solutions between 3 and 12. When determining the discoloration yields,the initial concentrations of dyes was considered for each pH, since the acidic pHs have a small effect on the initial concentration reduction of the dyes.

The low discoloration yields of dyes at acidic pH (Fig. 8) can be explained by the presence of competition between H^+ protons and dye ions (Chiou and Li, 2002). However, the MB decolorization yield is high at a neutral pH 7, These results are in agreement with those found by Poormand et al. (2017) and Rashed et al. (2016). For CR it is observed that the best yield is obtained at a pH of 5, the discoloration yield is very low in a very basic pH (11 and 12) and too acidic pH; in pH 3 and 4 the colorant CR changes its color and becomes purple, after contacting the composite sludge and alginate beads the fading yield is 0%. The decolorization yield of the dyes decreases at a pH greater than 10 this can be explained by the increase of the OH^- anions and the change in the surface charge of the adsorbent (Hameed et al., 2007).



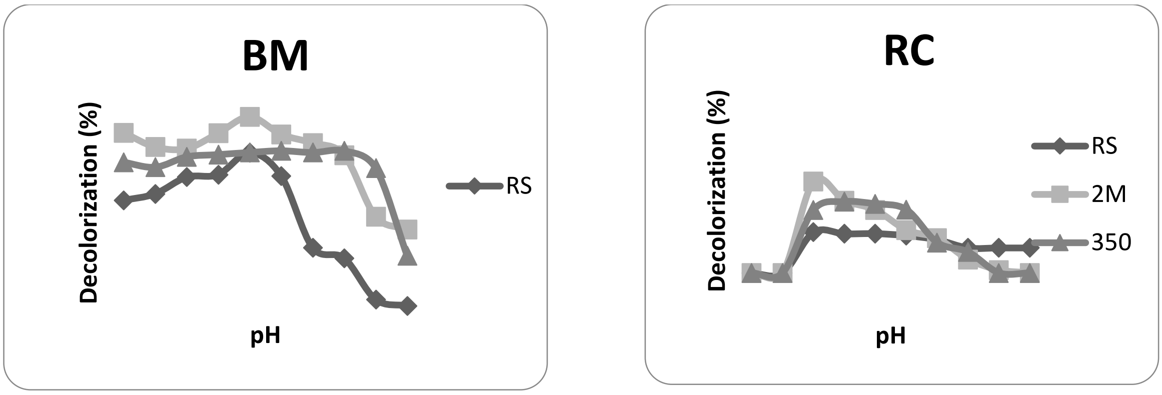
(c) (d)

Fig. 6. Kinetics of adsorption of MB and RC on composite beads (Ci dyes = 20mg/L, adsorbent mass 5g/L, ambient temperature, pHRC = 5.85, pHMB = 8.2): (a) represent the adsorption of MB, (b) represent the adsorption of CR



(c) (d)

Fig. 7. Effect adsorbent mass on the decolorization of MB and RC (Ci = 20mg/L, adsorbent mass 5g/L, ambient temperature, pHRC = 5.85, pHMB = 8.2, Time: 2h): (a) represent the adsorption of MB, (b) represent the adsorption of CR



(c) (d)

Fig. 8. Effect of pH on the decolorization of MB and RC (Ci = 20mg/L, T = 29°C, adsorbent mass 5g/L, Time: 2h): (a) represent the adsorption of MB, (b) represent the adsorption of CR

The decrease in the decolorization yield at pH 11 and 12 can also be explained by the melting of the composite beads due to the rupture of glycosidic bonds in a very basic medium (Palluault, 2010).

3.2.8. Kinetics of adsorption

Several models have been used to describe the kinetics of adsorption, in this study the kinetic model of the first order (Lagergren's equation) and on the kinetic model of the second order was used to describe the kinetics of adsorption of MB and of CR on composite alginate/hydroxide sludge beads.The calculated values of the adsorbed quantities Qe, the pseudo first and second order constants K_1 and K_2 and the regression coefficients R are given in Table1.

The results show that the values of R are very high for the second order model, they are all greater than 97% and exceed those obtained with the pseudo-first order model. Quantities fixed at equilibrium Qe for the pseudo-second-order model are close to the values found experimentally. So the adsorption process follows the pseudo-second order model well.

3.2.9. Adsorption isotherm

The Langmuir model better describes the adsorption of MB and CR by alginate and sludge composite and chemically and thermally activated sludge with a correlation factor that exceeds 90% for the three formulations for MB and CR decolorization. Adsorption is assumed to be monolayer and once a dye molecule occupies one site, no additional adsorption can occur at this site (Langmuir, 1918).

The maximum adsorbed quantities are very high for composite alginate and activated sludge beads with 2M sulfuric acid (125mg/g) (Table 2), this value is high compared to the results found by Rasheed et al. (2016) who reported that the maximum adsorbed quantity on sludge activated with 0.1M acetic acid is 70.4 mg/g

The values of the Langmuir separation factors belong to the range of validity (between 0 and 1), therefore the adsorptions of the two dyes are favorable. The values of n obtained by the Freundlich model are greater than 1 which confirms that the adsorption is favorable on the three formulations of composite beads (McKay et al., 1982).

The equilibrium time and the values of the maximum adsorbed quantities of the two dyes show that the MB adsorbs better to the composite beads with respect to the CR. These results are consistent with those of Li et al. (2015). Lunhong et al. (2011) found that the Langmuir model is suitable for describing MB adsorption equilibrium by composite magnetic beads of activated carbon/cobalt ferrite/alginate.

The maximum adsorbed amount of CR from activated sludge with 2M sulfuric acid is close to that found by Rashed (2011), who reported that adsorption of acid blue on sewage sludge follows the Langmuir model with adsorption capacity of 16.58 and 12.21 mg/g for washed sewage sludge and sludge activated carbon successively. Foroughi-Dahr et al. (2015) reported that adsorption of CR on tea waste follows the Langmuir model with a maximum adsorbed amount of 32.26 mg/g. Meroufel (2015) found that the maximum adsorption capacity of CR is 18.18mg/g on date kernels and 10.42mg/g on Calotropis Procera roots. The maximum adsorption capacities of CR on commercial Australian kaolins obtained by Vimonses et al. (2009) are 5.44, 6.81 and 7.27 mg/g.

Table1. Parameters of the 1st and 2nd order kinetic models

Dyes		***MB***			***CR***		
MODELS		***FORMULATION***			***FORMULATION***		
		RS	**350**	**2M**	**RS**	**350**	**2M**
Qexp (mg/g)		22.641	30.975	33.531	15.842	14.223	17.992
Pseudo-first-order	**K_1 (g/mg/min)**	0.023	0.016	0.018	0.014	0.007	0.012
	Qe calculeted (mg/g)	20.968	13.144	21.802	3.068	5.714	3.647
	R (%)	58.7	96.1	88.6	90	86.4	35.5
Pseudo-second order	**K_2 (g/mg/min)**	0.026	0.042	0.028	0.132	0.048	0.096
	Qe calculeted (mg/g)	23.810	32.258	35.714	15.873	12.821	17.857
	R (%)	97.7	99.3	98.5	99.8	98.4	99.1

Table 2. Parameters of Langmuir and Freundlich isotherms

Dyes		***MB***			***CR***		
MODELS		***FORMULATION***			***FORMULATION***		
		RS	**350**	**2M**	**RS**	**350**	**2M**
Langmuir	**Qm(mg/g)**	10.101	71.429	125	8;772	6.623	10.526
	K_L(L/mg)	2.152	0.452	0.250	1.966	2.188	2.111
	R_2	95.1	99.7	90.2	99.4	98.2	98.4
	R_L	0.848-0.016	0.998-0.078	0.699-0.618	0.822-0.024	0.813- 0.016	0.791-0.045
Freundlich	**K_f**	6.966	16.560	13.092	4.572	3.971	5.692
	1/n	0.324	0.302	0.212	0.494	0.415	0.658
	n	3.086	3.311	4.717	2.024	2.410	1.520
	R_2	78.2	14.9	84.6	90.7	89.6	92.1

4. Conclusions

This study focuses on sludge encapsulation using sodium alginates for the removal of two dyes; MB (basic cationics) and CR (anionic acid). The sludge underwent thermal and chemical activation, several formulations were prepared with different alginate/sludge ratios, The 1/5 ratio gives the best fading performance. The effect of two divalent (Ca^{2+} and Br^{2+}) and two trivalent (Fe^{3+} and Al^{3+}) crosslinkers was studied and the results show that the kinetics of calcium chloride are higher.

The effect of adsorption parameters such as: contact time, amount of adsorbent, pH, initial dye concentration and solution temperature have been studied and the results show that adsorption is maximum under : contact time of 5h, a pH of 7 for MB and 5 for CR, a mass of 10g/L of composite beads, concentration 20mg /L of dyes and at room temperature.

The mechanisms of adsorption of MB and CR can be described by a kinetics of the pseudo-second-order. The adsorption isotherms of MB and CR are described by the Langmuir model and the maximum adsorbed quantities by the alginate /raw sludge (RS), alginate / sludge activated at 350°C (350 °C) and alginate/sludge activated with 2M sulfuric acid (2M) are respectively 10.101mg/g, 71.429 mg/g and 125 mg/g for MB and 8.772 mg/g, 6.623 mg/g and 10.526 mg/g for CR.

By comparing the values of adsorbed quantities of the two dyes by the composite alginate/sludge beads, the adsorption on these composite materials is selective, they adsorb more cationic dyes than anionic dyes that can be attributed to the molecular weight and the size of the two dyes.

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