Journal of Environmental Management 218 (2018) 562–568

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Design and testing of a pilot scale magnetic separator for the treatment of textile dyeing wastewater

Tobías Salinas [a], Ignacio Durruty [b], Lorena Arciniegas [c], Gustavo Pasquevich [e], Matías Lanfranconi [a], Isabela Orsi [a], Vera Alvarez [a], Sebastian Bonanni [d, *]

[a] División Materiales Compuestos Termoplásticos, INTEMA (Conicet), Colón, 10890, Mar del Plata, 7600, Argentina
[b] Grupo de Ingeniería Bioquímica, Facultad de Ingeniería UNMdP, Juan B. Justo, 4302, Mar del Plata, 7600, Argentina
[c] División Polímeros Nanoestructurados, INTEMA (Conicet), Colón, 10890, Mar del Plata, 7600, Argentina
[d] División Ingeniería de interfases y bioprocesos, INTEMA (Conicet), Colón, 10890, Mar del Plata, 7600, Argentina
[e] Instituto de Física La Plata (IFLP), Calle 49 y 115, La Plata, 1900, Argentina

ARTICLE INFO

Article history:
Received 11 January 2018
Received in revised form
12 April 2018
Accepted 22 April 2018

Keywords:
Bentonite
Magnetic clays
Dye removal
Magnetic separator
Pilot scale

ABSTRACT

Iron nanoparticles can be incorporated on the structure of natural clays to obtain magnetic clays, an adsorbent that be easily removed from a wastewater by magnetic means. Magnetic clays have high adsorption capacities of different contaminants such as heavy metals, fungicides, aromatic compounds and colorants and show rapid adsorption kinetics, but crucial data for achieving its full or pilot scale application is still lacking. In this work, magnetic bentonites with different amounts of magnetite (iron fractions on the clay of 0.55, 0.6 and 0.6) were used to remove color from a real textile wastewater. On a first stage the optimal conditions for the adsorption of the dye, including pH, temperature and clay dosage were determined. Also design parameters for the separation process such as residence time, distance from magnet to magnetic clay and magnet strength were obtained. Finally a pilot scale magnetic drum separator was constructed and tested. A removal of 60% of the dye from a wastewater that contained more than 250 ppm of azo dye was achieved with only 10 min of residence time inside the separator.

1. Introduction

The release of chemical dyes and other hazardous chemicals by the textile industry poses serious and immediate threats to both ecosystems and human health (Greenpeace International, 2011). The textile industry produces large volumes of wastewater from different steps in the dyeing and finishing processes. Textile wastewater is often rich in color, contains residues of reactive dyes and chemicals and has high chemical and biological oxygen demands (COD and BOD) as well as several recalcitrant compounds (Verma et al., 2012; Lin and Chen, 1997).

Due to the complexity of the textile industry wastewater, the treatment process often includes several steps mainly focused on the reduction of BOD and COD and the discoloration of the waste. Many processes have been adapted to treat the wastewater produced by the textile dyeing process, including biological treatment (Sarayu and Sandhya, 2012), adsorption (Yagub et al., 2014), coagulation and flocculation (Verma et al., 2012) advanced oxidation techniques (Abo-Farha, 2010; Akpan and Hameed, 2010; Kumar and Rao, 2017), membrane filtration (Ciardell et al., 2001) and a combination of these processes.

Adsorption is widely used on the removal of chemical contaminants from waters due to its flexibility and simplicity. Current work is focused on the search of cost effective adsorbents, with those derived from natural materials being particularly attractive (Yagub et al., 2014; Ali et al., 2012; Babel and Kurniawan, 2003). In recent years, there has been an increasing interest in the use of raw clay materials (kaolinite, diatomite, bentonite and Fuller's earth) as adsorbents of different inorganic and organic contaminants, including heavy metals (Babel and Kurniawan, 2003), amino acids (Fushan et al., 1997), phenols and chlorophenols (Lee et al., 1997; Lawrence et al., 1998) and chemical dyes (Abo-Farha, 2010).

Clays have a layered structure with exchangeable ions on its structure and act as natural scavenger of charged molecules through ion exchange and adsorption. They also possess large

* Corresponding author.
E-mail address: Sebastian.bonanni@fi.mdp.edu.ar (S. Bonanni).

https://doi.org/10.1016/j.jenvman.2018.04.096
0301-4797/

surface areas ranging up to 800 m^2g^{-1} (Ali et al., 2012), and high removal efficiencies have been demonstrated for different contaminants (Yagub et al., 2014). They can be applied on fixed or fluidized bed columns, systems that show bed saturation, frequent replacement of the adsorbent (or the need for adsorbent regeneration) and high pressure drops as main drawbacks. Due to its micrometric size, clay particles require large times to settle and are not suitable either for separation by sedimentation (Akther et al., 2008; Roussy et al., 2005). Thus, structural and chemical modifications of natural clays are being studied aiming at lowering the settling time of this adsorbent and its flocculation capability (Roussy et al., 2005; Divakaran and Sivasankara, 2001; Chatterjee et al., 2009) One of the most promising modifications of natural clays is the addition of magnetic iron oxides nanoparticles (Oliveira et al., 2003). With this modification, the adsorption features of clays and the magnetic properties of iron oxides are combined to produce magnetic clays, an adsorbent that can be easily removed from the medium by magnetic separation (Ambashta and Sillanpaa, 2010).

As recently reviewed (Chen et al., 2016), magnetic clays have been tested at lab scale on the adsorption of several contaminants including heavy metals (Oliveira et al., Giakisikli and Anthemidis, 2013), herbicides (Liu et al., 2014), pesticides (Ouali et al., 2015) aromatic compounds, humic acids (Peng et al., 2006) and crude oil (Hsu et al., 2010), among others. The removal of colorants such as methylene blue (Chang et al., 2016; Cottet et al., 2014; Tireli et al., 2014) and solutions of organic dyes such as methyl orange (Yu and Yang, 2010), acid red (Hashemian, 2015) and acid blue (Özcan et al., 2005) has been also analyzed. Experimental conditions that maximize the adsorption of the contaminants (clay dosage, contact time, pH, and temperature) have been determined, kinetic parameters have been calculated for different combinations of contaminants and adsorbents and the regeneration of modified clays for its reuse after the adsorption was investigated (Lou et al., 2017; Jiang et al., 2018). Despite all this progress, research is still on a laboratory scale and crucial data for achieving full or pilot scale application of magnetizable clays on wastewater treatment is lacking.

In this work, useful parameters for the design of a magnetic separation process of the magnetic clay from the wastewater were obtained. The optimal pH and clay dosage for the removal of color were determined. The effect of the magnetite content of the clay on the separation time were experimentally and analytically analyzed. The magnetic properties of the clays were determined and the time required to separate the clay particles by magnetic means was compared with that of gravity separation, for different particles sizes and magnet geometries. Also magnetic force profiles were estimated and the maximum allowable distance between the array of magnets and the clay particles for achieving efficient separation was analytically estimated. Finally, with the obtained results a pilot-scale magnetic drum separator was designed and preliminary tested for the treatment of a real textile wastewater.

2. Experimental

2.1. Wastewater characteristics

Real textile wastewater was collected from local dyeing industry, stored at 5 °C and used upon one week after collection. Wastewater contained Direct Black 22 (chemical structure shown on Fig. S1 of the electronic supporting material, ESM), sodium chloride, and sodium carbonate and had a pH of 8.5. The amount of dye on the wastewater was determined by measuring its absorbance at 480 nm and using a calibration curve performed with aqueous Direct black solutions of known concentration.

2.2. Bentonite characterization and modification with iron oxides

Bentonite used in this work had a cation exchange capacity of 1.05 meq/g and was supplied by Minarmco S.A (Argentina). Iron oxide nanoparticles were obtained by mixing solutions of ferric chloride in water (20% m/V) and ferric sulfate in hydrochloric acid (0.6% m/V) and adding to the mixture 13% v/v of a solution containing 25% ammonium hydroxide. Final solution was slowly stirred for 10 min. Bentonite was swelled in distilled water at room temperature. Different quantities of nanoparticles solution were added (3 ml, 6 ml and 12 ml of magnetite solution per gram of clay for bentonites I, II and III respectively). The mixture was stirred for 2 h and then centrifuged. The precipitated solid was dried at 90 °C for 24 h, milled and sieved. Images of sieved clay particles were1 acquired with for measuring particle size (Fig. S2 on ESM). X-ray diffraction patterns of the raw clay and the modified clay were obtained to verify the presence of magnetite on the structure of the modified clay (Fig. S2). X-ray fluorescence was used to determine the fractions of chemical elements (higher than sodium) on each of the modified clays. Iron fraction on raw bentonite was 0.427, whereas for Bentonites I, II and III was 0.559, 0.604 and 0.652, due to the different magnetite contents of each clay. The complete composition of the bentonites is shown on ESM. The density of the clay was determined by compressing the powder with a hydraulic press obtaining 1 cm^3 samples that were weighed on an analytical balance. Density of the clays did not vary with the amount of magnetite added on the modification. Obtained density value was 2150 kg m^{-3} ± 160 kg m^{-3}. Magnetization (M) vs field (H) curves were performed to magnetic clays in a VSM magnetometer LakeShore 7004 at room temperature (Fig. S4 on ESM). Samples weight was around 100 mg. Specific saturation magnetization of 5.8, 8.5 and 17 Am^2/Kg were found for bentonites BI, BII and BIII respectively.

2.3. Wastewater discoloration assays

Batch assays were performed at different pH and clay dosages. The solution pH affects the adsorption of contaminants on the clay, since it alters the ionization of the dye molecule and the surface properties of the adsorbent (Yagub et al., 2014; Özcan et al., 2005; Ramakrishna and Viraraghavan, 1997). The pH was varied between 3 (the pH for magnetite dissolution) and 8.5 (raw wastewater pH) by addition of H_2SO_4 and NaOH solutions. Dosage of modified bentonite (BIII) on the samples was varied between 5 and 30 g per liter at different pHs. Wastewater samples with modified pH were transfer to a glass beaker and clay was added under constant agitation. A paddle stirrer was used, as stir bars would have attracted the magnetic adsorbent. After 10 min a sample of the liquid was taken and centrifuged for 5 min at 10,000 rpm. The fraction of dye removed from wastewater was determined by measuring samples absorbance at 480 nm (Durruty et al., 2015). Initial concentration of dye on the wastewater was 460 ppm. Temperature was kept constant at 25 °C during adsorption assays.

2.4. Settling tests

Settling time of the particles was evaluated with and without application of magnetic field on the sample. When the clay with the adsorbed dye settles, the wastewater is progressively discolored. Thus, absorbance of the wastewater can be used as an indicator of the progress of the settling process. The evolution of the absorbance of a sample containing wastewater and modified clay was

measured at a distance of 1.5 cm from the bottom of a recipient using a Hach DR890 portable colorimeter. The experimental setup and the relevant distances are shown on Fig. S5 on the ESM.

2.5. Calculation of forces acting on the magnetic particle during magnetic separation

When a magnetic clay particle is moving in a fluid towards a magnet, there are several forces acting on the particle, such as magnetic force, fluidic drag, particle/fluid interactions, buoyancy, thermal kinetics (brownian motion), gravity, and inter-particle interactions (magnetic dipole interactions) (Furlani and Ng, 2006). Due to the low particle concentration in the suspension, inter-particle effects and particle-fluid interactions were neglected. Brownian motion was neglected as the mean diameter of the particles was above its critical diameter (0.5 μm) (Gerber et al., 1983). Magnetic force on a magnetic clay particle produced by a cylindrical magnet was obtained by the effective dipole moment method (Jones, 1995) in which a magnetic particle is replaced by an equivalent point dipole (Furlani and Ng, 2008; Furlani, 2001).

In presence of the mentioned forces, the magnetic clays are accelerated until a limit velocity v_{lim} that equilibrates drag with the other forces acting on the particle is achieved (Bird, 2002). Transitory process for achieving the limit velocity were neglected and it was assumed that the particle was always moving at its limit velocity (see ESM for justification). However, due to the existence of a non-uniform magnetic gradient the limiting velocity depends on the position of the particle. In this case, to calculate position vs time for a single particle the elementary numeric Euler's method (Weisstein, Euler Forward Method on http://mathworld.wolfram.com/EulerForwardMethod.html), was used to solve the particle movement equation (see ESM).

2.6. Pilot scale magnetic separator

A pilot scale magnetic drum separator, was constructed and tested for the treatment of the textile wastewater. The operation diagram of the separator on an image of its operation can be found on the ESM. The separator consisted on a rotating drum with an external diameter of 0.2 m and a depth of 0.125 m, with an array of 50 neodymium magnets of 50 × 20 × 5 mm on its inner side. The drum was supported on a cylindrical plastic container by a metallic shaft. The distance between the bottom of the drum and the plastic container was 0.025 m. The net volume inside the separator was 0.82 L.

A wastewater with 250 ppm of dye was acidified to pH 3 and 10 g per liter of Bentonite III were added. After 10 min of continuous agitation, the wastewater was fed from a tank to the separator by an aquarium pump at a flowrate of 0.08 L per minute resulting in a residence time of approximately 10 min inside the separator. The drum was rotated at 2 rpm. The clay was separated from the drum with a plastic blade and recovered in a plastic container. Samples of the wastewater were taken before adding the clay (raw wastewater) and at the outlet of the magnetic separator. A sample of the outlet was centrifuged for 10 min at 5000 rpm to analyze the presence of unrecovered clay on the effluent. The concentration of dye on the samples was determined by measuring the absorbance at 480 nm and the use of a standard curve performed with known concentrations of Direct black dye.

3. Results and discussion

3.1. Adsorption of dye at different pHs and clay dosages

The effect pH and clay dosage on the dye removal was analyzed. In Fig. 1, fraction of dye removed from the wastewater at different experimental conditions is shown.

Bentonite is characterized by a three layer structure of two silicate layers enveloping an aluminate layer with an excess negative charge on the lattice that promotes the adsorption of positive charges (Ramakrishna and Viraraghavan, 1997). The adsorption of anionic dyes, such as direct black, is improved by lowering the pH as the protonation of amino groups increases the positive charge of the dye (Özcan et al., Özcan et al., 2005; Ramakrishna and Viraraghavan, 1997). As expected, the fraction of dye removed from the wastewater increases with decreasing pH. More than 80% of the dye is removed at pH 3 with a dosage of 10–30 g per liter of bentonite, in accordance with the removals of other dyes obtained with the same adsorbent (Chen et al., 2016). Interestingly, high fractions of dye are also removed at pH 5 with the highest bentonite dosage (30 g per liter).

Adsorption capacity of bentonite at different pHs, calculated from the variation on the concentration of dye on each condition, can be seen on Fig. 1C. Maximum adsorption per unit mass of bentonite is obtained at pH 3 with approximately 70 mg of dye absorbed per gram of bentonite with a dosage of 5 g per liter. This capacity is in the order of those reported for other dyes treated with clays and also for other sorbents used in dye removal (Yagub et al., 2014).

Direct dyes are applied at temperatures ranging from 70 to 90 °C (Ghaly et al., 2014) and wastewater is discharged at moderate temperatures. For determining if operating close to the discharge temperature would be beneficial for the adsorption process, the removal efficiency of the dye at 40 and 60 °C were determined.

Adsorption assays with 20 g l^{-1} of modified clay at pH 3 were repeated at 40 and 60 °C and removal efficiencies were 82.5 ± 0.4 and 86 ± 2.3% respectively (Fig. S12). Removal efficiency was negatively affected by an increase wastewater temperature as these values are lower than the removal efficiency obtained at ambient temperature (close to 90%). The negative effect of the increase in the temperature may be due to the exothermic nature of the adsorption process of azo dyes on bentonite (Toor and Jin, 2012). Adsorption isotherms, as well as complementary thermodynamic and kinetic analysis of the interaction between clays (raw and modified) and different dyes are beyond the aim of this work widely available on the bibliography (Kausar et al., 2018; Toor and Jin, 2012; Yagub et al., 2014).

From both an economical and operational point of view is crucial to minimize the amount of adsorbent needed on the process. Thus, according to results shown in Fig. 1, wastewater should be acidified prior to its treatment. Nevertheless, as a simplification of the treatment process is also desirable, with minimum or any modifications to the raw wastewater, an alternative approach may be to apply high clay dosages at neutral pH. A deeper analysis including economical and operational aspects has to be performed in order to identify the best option.

In order to reduce the operational costs of the treatment process, the magnetic adsorbent can be regenerated for its reuse (Lou et al., 2017; Jiang et al., 2018). Still a cheap regeneration process has to be identified for applying this approach at large scale. An alternative may be the utilization of the magnetic adsorbent on other applications such as the preparation of burnt bricks or other clay materials.

3.2. Settling of modified bentonites with and without magnetic field

Sedimentation is a simple solid-liquid separation process where the solid to be separated is allowed to settle and afterwards collected on the bottom of the tank (Edzwald, 2010). The time

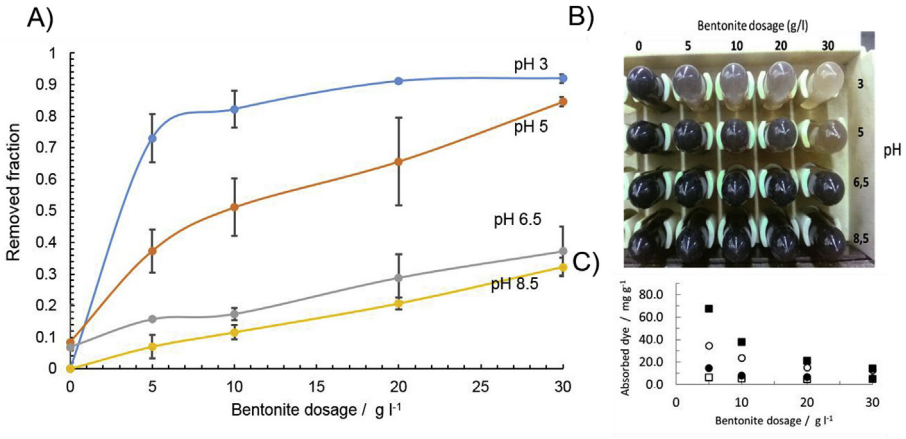

Fig. 1. A) Bentonite III dosage and pH effect on removal of dye from wastewater. Temperature was fixed at 25 °C and contact time between clay and wastewater was 10 min. B) Set of wastewater samples after treatment on conditions shown in A). C) Dye absorbed on the clay for different clay dosages at pH 3 (■), 5 (○), 6.5 (●) and 8.5 (□).

required for a particle to settle to the bottom of the sedimentation tank depends on the distance the particle has to travel as well as on the particle size. Clay particles are very small and its separation on sedimentation tanks would not be practical as they would require several hours to settle. For that reason the adsorption of contaminants on clays is usually performed on fixed bed columns that support the clay particles and through which wastewater is circulated (Auta and Hameed, 2014; Beall, 2003).

The objective behind the modification of the clays with magnetic particles is to lower the separation times required on traditional (sedimentation) separation. In this section, the reduction on the settling time will be quantified, for bentonites with different amount of magnetite on its structure.

Evolution of wastewater absorbance of a wastewater sample with modified bentonite with and without the application of a magnetic field was analyzed in order to evaluate to which extent the magnetic force accelerates the settling process of the modified clay (details on the experimental setup are found on Materials and Methods and ESM). Three types of bentonite, modified with different amounts of magnetite were used (3 ml, 6 ml and 12 ml of magnetite solution per gram of clay, called bentonites BI, BII and BIII, respectively). The magnetization of the clays increases with the amount of magnetite on the clay structure (Oliveira et al.) (Fig. S4). Thus bentonites with higher content of magnetite are expected to show a lower settling time.

When no magnetic field was applied only a small fraction of the clay (less than 10%) covered the distance to the sensor (1 cm) after 40 min (Fig. 2). With the application of a magnetic force the settling time is clearly reduced, with the final absorbance being achieved at about 15 min when using the bentonites of higher content of magnetite (Bentonite III). Also a clear variation between the settling times of the different bentonites was observed. The time required for half of the particles to reach the sensor was 2 min for Bentonite III, 2.8 min for Bentonite II and 13 min for Bentonite I. Although increasing modification costs of the raw material, increasing the amount of magnetite on the bentonite may be thus an interesting option in order to reduce the treatment time and consequently the volume required for the separation process.

3.3. Determination of design parameters for effective magnetic clay separation

The maximum distance through where a magnet can attract a magnetizable clay, the value of the magnetic force provided by magnet geometry, and its comparison with gravity force, and the time required for the separation to take place on the desired geometry must be determined for designing the magnetic separation process.

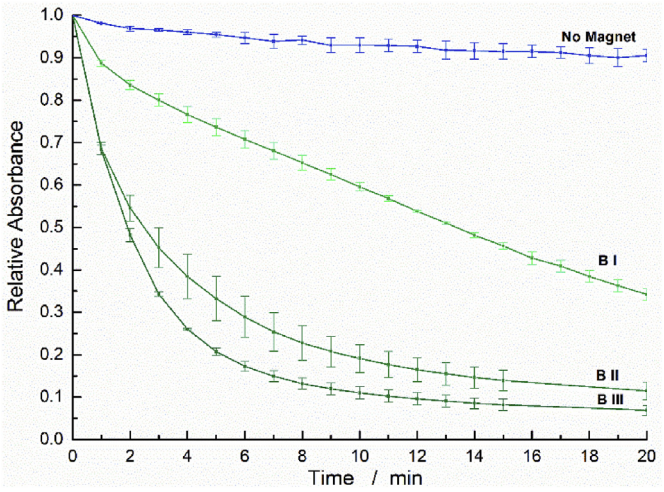

Fig. 2. Wastewater absorbance variation with time, at pH 3 for bentonite samples modified with 3 ml (BI), 6 ml (BII) and 12 ml (BIII) of magnetite solution per gram of clay. No magnet represents the average taken from BII and BIII measurements without applying a magnetic field.

The magnetic force distribution, and velocity profiles during magnetic separation were calculated following the approach detailed in ESM. The calculation method was validated by fitting the light-absorption vs time experimental results shown on the previous section. Simulation was qualitatively in good agreement with experimental results and particularly accurate for cases with more contents of magnetic nanoparticles (Bentonites II and III). Details about the simulation and experimental data fitting are given on the supplementary material.

While settling a bentonite particle of 6 μm diameter has limit velocity (see equation s(6) on ESM) of 0.08 m h^{-1}, thus requiring almost 40 min to cover a little distance of 0.05 m. When a magnetic field is applied, the settling time is reduced. In order to determine maximum allowable distance between the magnet and the bentonite particles on the separation process and the improvement on the settling time introduced by the presence of a magnetic field, the magnetic force acting on magnetic bentonite particles with different amount of magnetite and the velocity and distance

profiles were calculated.

A simple geometry consisting on a neodymium permanent magnet of cylindrical shape, 0.05 m diameter and 0.01 m height (residual magnetization Br 1.3 T) and a modified clay particle situated along the axis of the magnet was considered. For any other geometry, magnetic field intensity and gradient can be calculated following the approach described on materials and methods. The magnetic field decreases as the distance to the magnet increases (Furlani and Ng, 2006). For the mentioned geometry, it becomes negligible at distance higher than 0.05 m. Consequently, no magnetic force is exerted at such distance and the velocity of the modified clay particles (BI, BII and BIII) is almost equal to the one of the non-modified clay (no magnetite) (Fig. 3).

The magnetic force shows a maximum, and so does the velocity of the particles, at a distance of about 0.9 cm from the magnet. For bentonite BIII maximum magnetic force is about 28 times the sum of gravity and buoyancy forces (see Fig. S7). For bentonites BI and BII (with lower amount of magnetite), magnetic force is smaller, but still between 7 and 12 times higher than the gravity and buoyancy forces. As a consequence, settling velocities show a maximum of about 0.7, 1.2 and 2.25 m h^{-1} for bentonites BI, BII and BIII respectively (Fig. 3A). At distances between clay modified particles and magnet bigger than 0.05 m magnetic force has almost the same value of the sum of gravity and buoyancy forces and magnetic clay particles have approximately the same velocity as non-magnetic ones (0.06 m h^{-1}).

As mentioned above, for the considered geometry magnetic force is appreciable only at distances smaller than 0.05 m. Considering bigger initial distance from the magnet to the clay of 0.11 m, (from which the non-magnetic bentonite would take 4900 s to settle), the calculated settling time for bentonites I, II and III is 3200, 2950 and 2550 s, representing a reduction of only 35, 39 and 48%. On the other hand, when the initial distance is reduced to 0.02 m the settling time is reduced from 880 s for a non-magnetic bentonite to 114, 74 and 38 s for bentonites I, II and III, which represents a reduction of 87% for bentonite I, 92% for bentonite II and 96% for bentonite III. Distances profiles and percentages of reduction in settling time for other initial distances are shown in ESM.

Other important parameter on the design of the magnetic separation device is the intensity of the magnetic field (and its gradient) which can be varied by changing permanent magnet dimensions or the intensity of the current (and/or number of turns of the coil) in the case of an electromagnet. Increasing magnetic force allows the attraction of magnetic particles at larger distances, reducing separation time, but at the expense of increasing the cost of the separation equipment. An analysis of the influence of the dimensions of the magnet on the separation process can be found in the ESM.

3.4. Preliminary test of a pilot scale magnetic drum separator

The magnetic drum separators are the most frequently used equipment for wet low-intensity magnetic separation and are applied on the concentration of strongly magnetic ores, such as magnetite (Svoboda and Fujita, 2003). A peak magnetic field of 1.9 T, with very high gradient, can be generated on the surface of the drum by using permanent magnets made of rare earth compounds, such as neodymium (Oberteuffer, 1974).

The data acquired on the experimental work and calculations was used to design a pilot scale magnetic drum separator for the separation of magnetizable clay from the textile wastewater. The separator consisted on cylindrical plastic container and a plastic rotating drum with an array of neodymium permanent magnets on its inner side. The wastewater was continuously pumped to the separator and collected on the outlet. A preliminary testing of this equipment was performed for the separation of the magnetizable clay from the textile wastewater. Operating conditions are detailed on materials and methods and a diagram of the magnetic separator can be found on the ESM.

Samples at the inlet and outlet of the separator were analyzed to determine the concentration of dye. Also a sample from the outlet of the separator was centrifuged to check for unrecovered clay on the effluent. The dye concentration of this samples can be seen on Fig. 4.

With the magnetic drum separator it was possible to remove 62% of the dye content, achieving 92 ppm at the outlet with a residence time of 10 min on the separator. In the previous sections it was shown that a removal of more than 80% of the color can be achieved with the conditions used on the magnetic separator (pH 3, 10 g l^{-1} of clay, Fig. 1). This removal was obtained only after the centrifugation of the sample. The lower treatment efficiency on the separator can be explained by the presence of unrecovered clay at the outlet, which was observed on the centrifuged sample.

A higher residence time or the recirculation of the effluent to the inlet may thus increase the treatment efficiency of the separator. The effect of the rotating speed of the drum and the distance between the drum and the base of the separator should be analyzed in

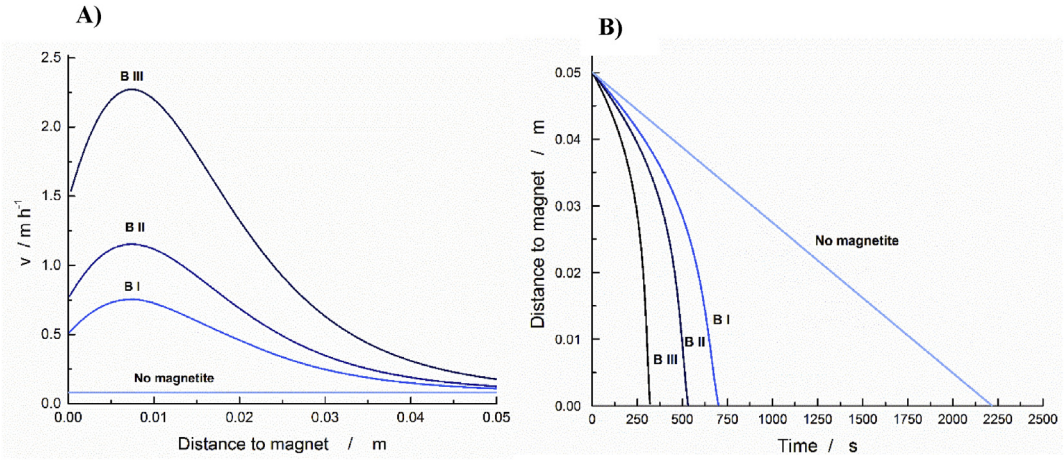

Fig. 3. A) Velocity variation with the distance to the magnet for 6 μm diameter particles and Bentonites I, II and III (BI, BII and BIII) and no magnetic bentonite (no magnetite). **B)** Relation between distance and time for the same system described in A), and an initial distance to the magnet of 0.05 m.

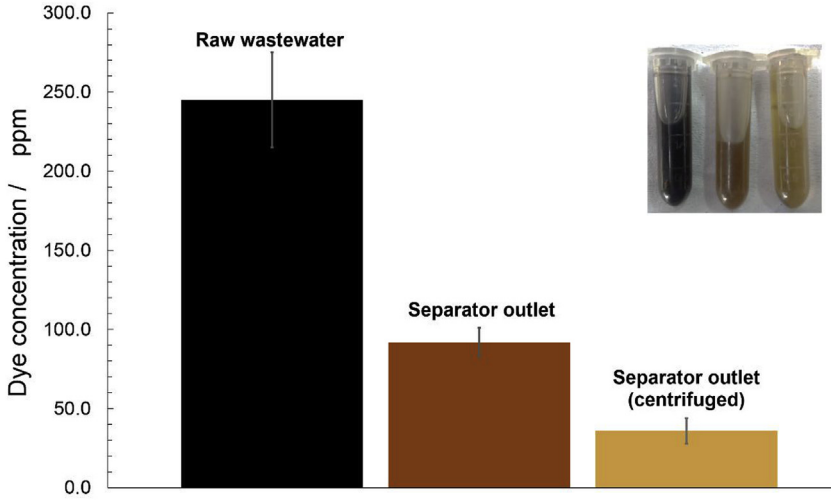

Fig. 4. a) Dye concentration of raw wastewater, at the outlet of the pilot scale magnetic separator and on a centrifuged sample from the outlet of the separator. Inlet wastewater pH was 3 and bentonite dosage was 10 g l^{-1}. A flowrate of 0.08 l min^{-1} was fed to the separator, resulting in a residence time of 10 min. The drum was rotated at 2 rpm. An operation diagram of the magnetic drum can be found on the ESM. Inset: samples of raw wastewater (left), separator outlet (center) and centrifuged separator outlet (right).

order to maximize the treatment efficiency. Despite this, the results show that magnetizable clays may be successfully applied on magnetic drums for the treatment of textile wastewater.

4. Conclusions

Magnetizable clays represent an interesting option for textile wastewater treatment. It was shown that real wastewaters colored with complex chemicals such as azo-dyes can be treated with relatively low dosages of clay. The pH of the wastewater is a key parameter on the adsorption process; with higher adsorptions obtained al lower pHs. Economical and life cycle analyses have to be performed for determining if either the acidification of the wastewater for reducing the required adsorbent dosage or, alternatively, the use of higher amounts of adsorbent at raw pH is the best strategy for a real scale treatment. Besides its great adsorption capacity, the main advantage of the magnetizable clays relies on the simplicity of the separation of the adsorbent by magnetic means. The challenge for its application at large scale resides on the design of the separation process. It was shown on this work that when using commercially available permanent magnets, magnetic forces acting on the clay particles are higher than competing forces only at distances of a few centimeters from the magnet. For that reason, efficient separation will be only obtained for processes with short distances between the magnets and the clay particles during the separation. It was also shown that increasing the amount of magnetite on the bentonite particles reduces the separation time of the adsorbent. It is clear that in any process aimed at separating the magnetic particles from the wastewater the distance between the magnets and the clay should be limited to the centimeter scale, where great reduction on the separation time (almost 90%) can be achieved.

Magnetic drum separators can offer minimal distances between the magnets and the wastewater. A preliminary test of a pilot-scale magnetic separator shown that magnetizable clays can be successfully applied for wastewater treatment on magnetic drum separators, achieving acceptable color removal efficiencies. The treatment efficiency might be enhanced by recirculating the effluent to increase the residence time on the separator. Alternatively, the rotary drum may serve as a pre-treatment for lowering the contaminant load of classical treatments such as biological degradation in aerobic and aerobic digesters or constructed wetlands.

Declarations of interest

None.

Acknowledgements

The authors thank Melina Bracone, Valeria Giunta and Vanesa Fuchs for their technical support. The work was supported by Fundación Argentina de Nanotecnología (FAN) and by Agencia Nacional de Promoción Científica y Técnica (ANPCyT) by PICT 2015-0094. Sebastian Bonanni, Ignacio Durruty, Gustavo Pasquevich and Vera Alvarez are researchers of The National Scientific and Technical Research Council of Argentina (CONICET).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jenvman.2018.04.096.

References

Abo-Farha, S., 2010. Comparative study of oxidation of some azo dyes by different advanced oxidation processes: fenton, Fenton-like, photo-Fenton and photo-Fenton-like. J. Am. Sci. 6 (10), 128–142.
Akpan, U.G., Hameed, B.H., 2010. Parameters affecting the photocatalytic degradation of dyes using TiO2-based photocatalysts: a review. J. Hazard. Mater. 170 (2–3), 520–529.
Akther, S., Hwang, J., Lee, H., 2008. Sedimentation characteristics of two commercial bentonites in aqueous suspensions. Clay Miner. 43 (3), 449–457.
Ali, I., Asim, M., Khan, T.A., 2012. Low cost adsorbents for the removal of organic pollutants from wastewater. J. Environ. Manag. 113, 170–183.
Ambashta, R.D., Sillanpää, M., 2010. Water purification using magnetic assistance: a review. J. Hazard. Mater. 180 (1), 38–49.
Auta, M., Hameed, B.H., 2014. Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. Chem. Eng. J. 237, 352–361.
Babel, S., Kurniawan, T.A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J. Hazard. Mater. 97 (1), 219–243.
Beall, G.W., 2003. The use of organo-clays in water treatment. Appl. Clay Sci. 24, 11–20.
Bird, R.B., 2002. Transport phenomena. Appl. Mech. Rev. 55 (1), R1–R4.
Chang, J., Ma, J., Ma, Q., Zhang, D., Qiao, N., Hu, M., Ma, H., 2016. Adsorption of methylene blue onto Fe3O4/activated montmorillonite nanocomposite. Appl. Clay Sci. 119, 132–140.

Chatterjee, T., Chatterjee, S., Woo, S.H., 2009. Enhanced coagulation of bentonite particles in water by a modified chitosan biopolymer. Chem. Eng. J. 148 (2), 414–419.
Chen, L., Zhou, C.H., Fiore, S., Tong, D.S., Zhang, H., Li, C.S., Ji, S.F., Yu, W.H., 2016. Functional magnetic nanoparticle/clay mineral nanocomposites: preparation, magnetism and versatile applications. Appl. Clay Sci. 127–128, 143–163.
Ciardell, G., Corsi, L., Marcucci, M., 2001. Membrane separation for wastewater reuse in the textile industry. Resour. Conserv. Recycl. 31 (2), 189–197.
Cottet, L., Almeida, C., Naidek, N., Viante, M., Lopes, M., Debacher, M., 2014. Adsorption characteristics of montmorillonite clay modified with iron oxide with respect to methylene blue in aqueous media. Appl. Clay Sci. 95, 25–31.
Divakaran, R., Sivasankara Pillai, V.N., 2001. Flocculation of kaolinite suspensions in water by chitosan. Water Res. 35 (16), 3904–3908.
Durruty, I., Fasce, D., González, J.F., Wolski, E.A., 2015. A kinetic study of textile dyeing wastewater degradation by Penicillium chrysogenum. Bioproc Biosyst. Eng. 38 (6), 1019–1031.
Edzwald, J.K., 2010. Water Quality and Treatment a Handbook on Drinking Water. McGrawHill, New York.
Furlani, E.P., Ng, K.C., 2006. Analytical model of magnetic nanoparticle transport and capture in the microvasculature. Phys. Rev. E 73 (6), 61919.
Furlani, E.P., Ng, K.C., 2008. Nanoscale magnetic biotransport with application to magnetofection. Phys. Rev. E 77 (6), 61914.
Furlani, E.P., 2001. Permanent Magnet and Electromechanical Devices; Materials, Analysis and Applications. Academic Press, San Diego.
Fushan, M., Shiwer, W., Yongning, Q., Xiao, W., 1997. Adsorption of amino acid by bentonite, ion exchange and adsorption. Lizi Jiaohuan Yu Xifu 13, 54–59.
Ghaly, A.E., Ananthashankar, R., Alhattab, M.V.V.R., Ramakrishnan, V.V., 2014. Production, characterization and treatment of textile effluents: a critical review. J. Chem. Eng. Process Technol. 5 (1), 1–18.
Gerber, R., Takayasu, M., Friedlander, F.J., 1983. Generalization of HGMS theory: the capture of ultrafine particles. IEEE Trans. Magn 19 (5), 2115–2117.
Giakisikli, G., Anthemidis, A.N., 2013. Magnetic materials as sorbents for metal/metalloid preconcentration and/or separation. A review. Anal. Chim. acta 789, 1–16.
Greenpeace International, 2011. Dirty Laundry: Unravelling the Corporate Connections to Toxic Water Pollution in China. Greenpeace international, Amsterdam.
Hashemian, S., 2015. MnFe2O4/bentonite nanocomposite as a novel magnetic material for adsorption of acid red 138. Afr. J. Biotechnol. 9 (50), 8667–8671.
Hsu, R.S., Chang, W.H., Lin, J.J., 2010. Nanohybrids of magnetic iron-oxide particles in hydrophobic organoclays for oil recovery. ACS Appl. Mater. interfac 2 (5), 1349–1354.
Jiang, L., Ye, Q., Chen, J., Chen, Z., Gu, Y., 2018. Preparation of magnetically recoverable bentonite–Fe3O4–MnO2 composite particles for Cd (II) removal from aqueous solutions. J. Colloid Interfac Sci. 513, 748–759.
Jones, T.P., 1995. Electromechanics of Particles. Cambridge University Press, Cambridge.
Kausar, A., Iqbal, M., Javed, A., Aftab, K., Bhatti, H.N., Nouren, S., 2018. Dyes adsorption using clay and modified clay: a review. J. Mol. Liq. 256, 395–407.
Kumar, S.G., Rao, K.K., 2017. Comparison of modification strategies towards enhanced charge Carrier separation and photocatalytic degradation activity of metal oxide semiconductors (TiO2, WO3 and ZnO). Appl. Surf. Sci. 391, 124–148.
Lawrence, M.A., Kukkadapu, R.K., Boyd, S.A., 1998. Adsorption of phenol and chlorinated phenols from aqueous solution by tetramethylammonium-and tetramethylphosphonium-exchanged montmorillonite. Appl. Clay Sci. 13 (1), 13–20.
Lee, J.H., Song, D.I., Jeon, Y.W., 1997. Adsorption of organic phenols onto dual organic cation montmorillonite from water. Sep. Sci. Technol. 32 (12), 1975–1992.
Lin, S.H., Chen, M.L., 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res. 31 (4), 868–876.
Liu, H., Chen, W., Liu, C., Liu, Y., Dong, C., 2014. Magnetic mesoporous clay adsorbent: preparation, characterization and adsorption capacity for atrazine. Microporous Mesoporous Mater. 194, 72–78.
Lou, Z., Zhang, W., Hu, X., Zhang, H., 2017. Synthesis of a novel functional group-bridged magnetized bentonite adsorbent: characterization, kinetics, isotherm, thermodynamics and regeneration. Chin. J. Chem. Eng. 25 (5), 587–594.
Oberteuffer, J., 1974. Magnetic separation: a review of principles, devices, and applications. IEEE Trans. Magn 10 (2), 223–238.
Oliveira, L.C., Rios, R.V., Fabris, J.D., Sapag, K., Garg, V.K., Lago, R.M., 2003. Clay–iron oxide magnetic composites for the adsorption of contaminants in water. Appl. Clay Sci. 22 (4), 169–177.
Ouali, A., Belaroui, L.S., Bengueddach, A., Galindo, A.L., Peña, A., 2015. Fe2O3–palygorskite nanoparticles, efficient adsorbates for pesticide removal. Appl. Clay Sci. 115, 67–75.
Özcan, A.S., Erdem, B., Özcan, A., 2005. Adsorption of acid blue 193 from aqueous solutions onto BTMA-bentonite. Colloids Surfaces A Physicochem. Eng. Aspects 266 (1), 73–81.
Peng, X., Luan, Z., Zhang, H., 2006. Montmorillonite–Cu (II)/Fe (III) oxides magnetic material as adsorbent for removal of humic acid and its thermal regeneration. Chemosphere 63 (2), 300–306.
Ramakrishna, K.R., Viraraghavan, T., 1997. Dye removal using low cost adsorbents. Water Sci. Technol. 36 (2), 189–196.
Roussy, J., Van Vooren, M., Dempsey, B.A., Guibal, E., 2005. Influence of chitosan characteristics on the coagulation and the flocculation of bentonite suspensions. Water Res. 39 (14), 3247–3258.
Sarayu, K., Sandhya, S., 2012. Current technologies for biological treatment of textile wastewater–a review. Appl. Biochem. Biotechnol. 167 (3), 645–661.
Svoboda, J., Fujita, T., 2003. Recent developments in magnetic methods of material separation. Miner. Eng. 16 (9), 785–792.
Tireli, A.A., Marcos, F.C.F., Oliveira, L.F., Guimarães, I.d.R., Guerreiro, M.C., Silva, J.P., 2014. Influence of magnetic field on the adsorption of organic compound by clays modified with iron. Appl. Clay Sci. 97–98, 1–7.
Toor, M., Jin, B., 2012. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chem. Eng. J. 187, 79–88.
Verma, A.K., Dash, R.R., Bhunia, P., 2012. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. J. Environ. Manag. 93 (1), 154–168.
Weisstein E.W., Euler Forward Method, From MathWorld–A Wolfram Web Resource. http://mathworld.wolfram.com/EulerForwardMethod.html.
Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M., 2014. Dye and its removal from aqueous solution by adsorption: a review. Adv. Colloid Interface Sci. 209, 172–184.
Yu, J., Yang, Q.X., 2010. Magnetization improvement of Fe-pillared clay with application of polyetheramine. Appl. Clay Sci. 48 (1), 185–190.