

Separation of dyes from aqueous systems by magnetic alginate beads

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ABSTRACT

This study deals with the development of a clean process for the remediation of waters polluted with the dyes methylene blue (MB) and methyl orange (MO). Magnetic adsorbents have been synthesized in order to develop an extraction process assisted by a magnetic field to avoid extra separation techniques. To follow an “ecoconception” approach, magnetic beads containing magnetite were prepared with sodium alginate. Alginates are natural polysaccharides present in marine seaweed. Batch experiments were carried out as a function of initial pH solution, mass of adsorbent, initial dye concentration, salinity and desorption. An optimum adsorption was observed at pH 7 and 4 for MB and MO, respectively. The maximum adsorption followed the Langmuir, Freundlich and Dubinin Radushkevich isotherms with a value of 10,851.64 mg of MB per gram of adsorbent, whereas MO presented a value of 58,411.21 mg/g. Electrostatic interactions are suggested as the driving adsorption forces based on the equilibrium, salinity and desorption results. Salinity has a negative impact on MB due to competing ions and a positive effect on MO, due to shielding of equally charged groups. Acetone was the most efficient eluent for MO and HCl for MB. This present work highlights the potential use of magnetic beads in the elimination of dyes from wastewater as a low-cost and environment friendly purification technique.

KEYWORDS: adsorption, magnetic beads, alginate, isotherm, pH, desorption

INTRODUCTION

Industrial colored waters from food, pharmaceutical and textile factories are the most difficult wastewaters to treat. This is due to the synthetic origin of the dyes that are used. Their complex structure includes aromatic molecules which makes them more stable and not degradable even under strong oxidizing conditions [1]. Approximately 100,000 commercially available known dyes are sold, covering a total production of 7×10^5 metric tons per year in the world. According to their properties, they can be classified as acidic, basic and neutral [2, 3].

The low degradation of these synthetic dyes makes the conventional biological treatments inefficient to remediate this contamination [4]. Colored waters are generally treated by means of physical and chemical procedures [5]. These techniques include physicochemical flocculation combined with flotation, membrane filtration, ionic exchange, irradiation, and precipitation. Nevertheless, these technologies are usually not very efficient, are expensive and do not adapt easily to a broad range of colored residual waters.

Bioremediation is the term applied to the decontamination of water or soil by using biochemical, chemical or physical processes. Bioremediation is divided into two main fields: biosorption and bioaccumulation [6]. Biosorption, which can be thought like “adsorption by biological adsorbents”,

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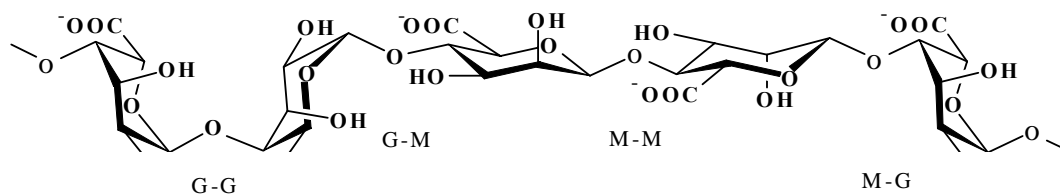


Figure 1. Sequence of the polymeric alginate chain showing the different mannuronic (M) and guluronic (G) blocks.

offers advantages like low-cost operations, reduction of the chemical and biological sludges that would need special disposal. It is also cheaper, highly efficient, and selective towards certain types of contaminants. Biosorption also allows the regeneration of the biosorbent for consecutive cycles and the recovery of the pollutant in case of precious metals.

Marine algae have successfully been used in the past as biosorbents of inorganic and organic pollutants [7-9]. The high adsorption capacity of algae is thought to be due to the presence of functional groups with high electron density, mainly alginate. Since the concentration of alginate is much higher than any other component in algae, they are the most active centers for adsorption of pollutants. Alginates are, chemically speaking, polymers of a family of lineal polysaccharides composed by units of mannuronic (M) and guluronic (G) acids. These units are randomly arranged in the polymer of alginate, alternating the sequences MM, GG, MG, and GM as shown in Figure 1. This peculiar geometry allows the gelification of alginates in the presence of calcium ions and/or some divalent metals [10].

The gelification or cross-linkage property of alginates in the presence of calcium ions is extremely important and advantageous. It has been demonstrated that Ca (II) ions cross-link the alginate chains, enhancing the mechanical properties following the egg box model [10] (Figure 2). Previous studies have shown that cross-linked alginates are thermally more stable than non-treated alginates and also more resistant towards corrosive reagents [11]. This time, the cross-linkage of alginate has been coupled to the encapsulation of magnetic particles to facilitate their separation from the solution. The porosity of alginate beads maximizes the specific surface of the adsorbent by making the active sites

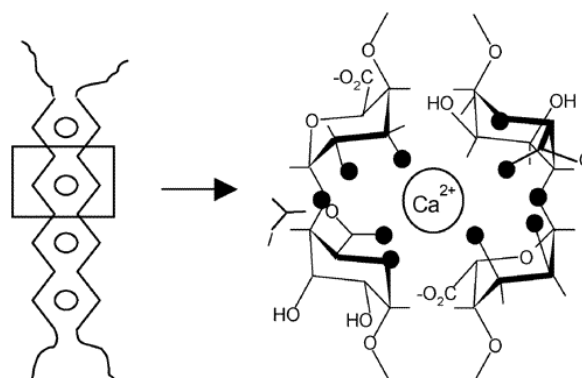


Figure 2. Cross-linkage of two alginate chain by calcium (II) ions, following the Egg Box model.

more accessible. Meanwhile, the cross-linkage enhances the mechanical and thermal resistance; and the encapsulated magnetite accelerates the separation of the beads from the solution by using a simple electromagnet.

Very few studies have been conducted with porous adsorbents and even fewer by encapsulating magnetite in the adsorbents [12]. Therefore, the present study is aimed at investigating the interaction of two synthetic dyes: Methylene Blue (MB) and Methyl Orange (MO) as basic and acidic dyes, respectively. The equilibrium state of the adsorption of these dyes was investigated to optimize the process as a function of pH, salinity, adsorbent dose and dye concentration. Finally, an extensive and elucidating desorption experiment revealed that the dyes can be recovered.

MATERIALS AND METHODS

Reagents and solutions

Stock solutions of MB and MO were prepared by dissolving both dyes (Reagent grade, Sigma-Aldrich) in deionized water. Solutions of varying concentrations

were prepared by dilution of the stock solution until the desired concentration was reached. MO has a lower solubility and the stock solution had to be constantly re-dissolved by sonication. The initial pH was measured with a pH-meter (Fisher Scientific Accumet Model AB15) and adjusted to the required pH values by adding aliquots of 0.1 M HCl and 0.1 M NaOH prior to contact with the adsorbent.

Preparation of magnetite

The conventional procedure of preparation (Scheme 1) of magnetite involves the stoichiometric combination of Fe (III) and Fe (II) chlorides (reagent grade, Sigma-Aldrich) under agitation for 10 minutes [13]. Then, a solution of NH_4OH is added dropwise to the mixture. The formation of a black solid indicated the formation of magnetite. NH_4OH is added until no further precipitation is seen. Then, the solution is decanted and the black solid is vigorously rinsed with deionized water to neutral pH. The pH neutrality was monitored by litmus paper. The magnetite was oven-dried at not more than 60 °C overnight. The dried magnetite was then crushed in a mortar with a pestle, sieved and stored in a glass vial until usage.

Preparation of the magnetic alginate beads

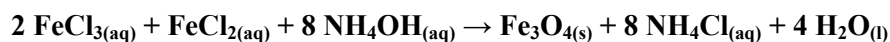
Several trials were carried out to find out the right magnetite/alginate proportion to optimize the magnetic properties of the beads. Excess of magnetite would minimize the content of alginate in the bead, and lower the adsorption. Conversely, too little magnetite in the bead would not respond to external magnets for their removal from the solution.

The procedure was as follows (Scheme 2): 3 grams of sodium alginate was dissolved in 100 mL of deionized water and heated at not more than 80 °C under constant agitation until complete dissolution of the alginate. In a separate beaker, 1 L of a solution of calcium chloride (CaCl_2) is prepared. 3 g of magnetite is added to the room-temperature solution of sodium alginate. Then, the suspension magnetite/alginate is added dropwise to the calcium chloride solution that is being agitated by a magnetic stirrer. The alginate beads are instantaneously formed encapsulating the magnetite particles. Later, the beads were vigorously rinsed with deionized water until the rinses did not show a precipitate with a solution of AgNO_3 . This test indicates the presence of chloride ions even at trace concentrations. The magnetic beads were stored in polyethylene bottles in water to avoid drying and stored in a refrigerator at 4 °C until usage.

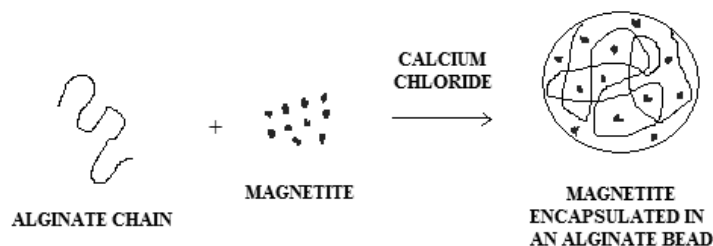
Mass ratio between the wet and dry beads was determined by drying the wet beads in an oven at 100 °C overnight. The results show that the mass ratio between wet and dry beads is 120:1.

Adsorption experiments

Duplicated batch adsorption experiments were carried out at room temperature by allowing an accurately weighed amount of the magnetic beads to reach equilibrium with MB and MO solutions of known concentrations. Initial concentrations of MB and MO were held between 0.1 and 6 mM. Due to its low solubility, MO was only studied up to 2 mM concentrations. The mixture was kept under



Scheme 1. Chemical reaction for the preparation of magnetite.



Scheme 2. Preparation of the magnetite-encapsulated alginate beads.

orbital agitation in an incubator shaker (New Brunswick Scientific Model I24) at 200 rpm for 20 h. The estimated adsorption time was determined by preliminary experiments. Thereafter, the suspensions were separated by a conventional magnet and the supernatant taken out. The concentration of the remaining solution of MB and MO was determined through UV-vis spectrophotometry using a microplate reader (Synergy 4, Biotek) at a wavelength of 660 and 460 nm for MB and MO, respectively.

Effect of initial solution pH

The initial pH of solutions was adjusted between 2 and 10 for MB. The solubility of MO decreased dramatically at pH values below 4; therefore for MO, the pH range was 4 to 10. Finally, 0.5 grams of magnetic beads were added to each solution.

Effect of mass of adsorbent and adsorption isotherms

A variable amount of magnetic beads (between 0.25 and 10 grams) was mixed with 50 mL solution volumes of MB and MO of variable concentrations in the range of 0.25 and 6 mM.

Effect of salinity

Taking into account the optimum parameters for initial solution pH, adsorbent dose and solution initial concentration, batch experiments were performed at different concentrations of sodium nitrate, NaNO₃ (reagent grade, Sigma-Aldrich) in the range 0.01 and 0.25 M solutions of NaNO₃. The low solubility of both dyes in the presence of high salt concentration avoided the studies at higher salinity. The goal of this study is to investigate the interference of ions like Na⁺ and NO₃⁻ as competitive ions of both dyes for the adsorption sites of the magnetic beads.

Desorption experiments

Considering the optimum values of mass, initial pH, concentration and salinity, a bigger scale experiment was carried out to obtain dye-loaded magnetic beads. The beads were extracted, rinsed with the minimum amount of deionized water to just remove any excess of the dye solution and air dried for 1 hour. Then, 0.6 grams of the dye-loaded magnetic beads were put in contact with 20 mL of cosolvents for 4 hours to identify the

best desorbing solution. A wide range of cosolvents were used to explore the best conditions to recycle the beads and also concentrate the dyes in a smaller volume. The cosolvents included solutions of deionized water, 30% v/v ethanol, 30% v/v acetone, 0.1 M HCl, 0.1 M NaCl, 0.1 M NaOH, 0.1 M NaNO₃, and 0.1 M CaCl₂. Acetone and ethanol were used to explore if slightly hydrophobic solvent are able to remove the dyes. Acids and bases were basically used to test the effect of pH on desorption. The rest of cosolvents were selected based on their salinity and ionic size properties. In the case of calcium chloride, it was used to evaluate the stability of the complex dye/alginate compared to the egg model structure that alginate would gain by incorporating the calcium divalent ions.

Data analysis

The removed quantity of dye by the magnetic beads expressed as Adsorption Capacity (*q*) in mg per g of dry adsorbent was calculated using the formula in Equation (1):

$$q = \frac{(C_i - C_{eq}) * V}{m} \quad (1)$$

where *m* is the mass of the adsorbent expressed in g, *V* is the volume of the solution in L and *C_i* and *C_{eq}* are the initial and the equilibrium concentrations of MB and MO expressed in mg/L, respectively.

An alternative way of expressing the adsorption and desorption properties of the adsorbent is as Adsorption Percentage (%ADS) or Desorption Percentage (%DES) which only consider the initial and remaining dye concentration in solution. It is defined by the formula in Equation (2):

$$\% \text{ ADS} = \frac{(C_i - C_{eq}) \times 100}{C_i} \quad (2)$$

RESULTS AND DISCUSSION

Effect of solution initial pH

The dependence on the pH is one of the most important factors in the adsorption of environmental contaminants in aqueous solutions since it influences the solution chemistry of dyes or any other organic/inorganic pollutant (i.e. hydrolysis, redox reactions, polymerization and complexation). pH also has a

strong influence on the speciation and the sorption availability of dye compounds as well as the ionic state of functional groups on the surface of adsorbents [14].

Figure 3 shows the effect of solution pH on the adsorption of MB and MO at room temperature. Both dyes report a completely different pH adsorption curves with maximum q values around 3,750 mg/g and 1,050 mg/g for MB and MO, respectively. These results can be explained based on the electrostatic attraction/repulsion. Previous studies [15] demonstrated that alginates in algae have apparent ionization constants around 3.0 whereas at higher pH values, the alginates are negatively charged. The results from Figure 3 are completely in agreement with the chemical properties of the dyes and the alginate.

As seen in Figure 4, MB is an organic base that is pH sensitive and has a permanent positive charge. This permanent positive charge is actually responsible for the high affinity between alginates and MB. At low pH values, this adsorption is dramatically decreased, especially at pH lower than 3 where the alginate is protonated (becoming alginic acid) and the electrostatic interaction with MB disappears. From the pH studies we can anticipate that the adsorption between MB and the beads is mainly electrostatic because the adsorption is not affected up to pH 10. This means that MB will be adsorbed on alginate as long as it holds a negative charge. Therefore alginate is a good adsorbent for MB due to the broad pH range where the adsorption is constant at its highest value.

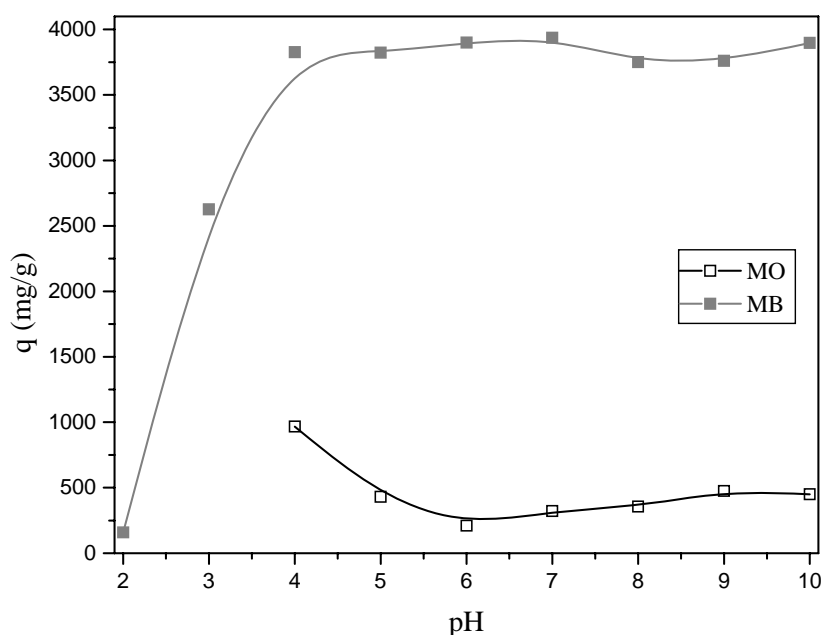


Figure 3. Effect of pH on MB and MO adsorption by magnetic alginate beads.

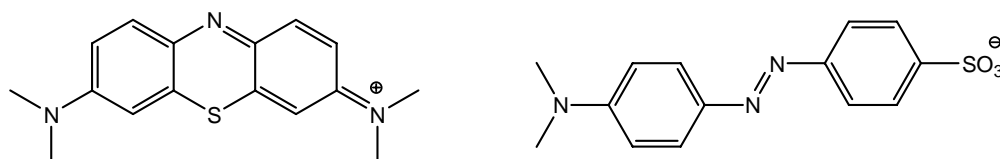


Figure 4. Chemical structures of MB (left) and MO (right).

On the other hand, MO, as seen in Figure 4, is an acid and therefore will hold a negative charge at pH values higher than its pK_a . MO has a pK_a [16] (acid dissociation constant) of 3.5, which means that at pH values higher than 3.5, MO will be negatively charged and neutral at lower pHs. This also explains the low experimental solubility of MO at pH values lower than 4.0. MO is only soluble in water when it is negatively charged. Once MO becomes protonated the hydrophobic properties of the molecule and the absence of a charge to keep it in solution, promote its precipitation. The adsorption is also greatly affected by the pH because the negative charges of the alginate at pH values higher than 3 will repel the negative charge of MO at pH higher than 3.5. The maximum adsorption of MO observed at pH 4 reflects the most extreme conditions where the adsorption can handle the repulsion between both negative charges that are being generated in the system. At higher pH values, the negatively charged population of MO and alginate would be too large to handle. Lowering the pH accommodates the adsorption by having less species with a negative charge. As expected, the adsorption capacity of MO is much lower than MB due to its chemical nature.

This electrostatic behavior has also been observed in the adsorption of heavy metals on alginates (algae).

In that case, it was postulated that the negative charge of the alginates was crucial for the adsorption of copper (II) [17] and lead (II) [18] ions. As observed in this case, adsorption of both heavy metals was almost negligible at pH values below 3.0.

Based on these results, we propose an electrostatic adsorption of MB and MO on magnetic alginate beads, which is strongly governed by the pH ionization of the functional groups on the adsorbent and on the dyes.

Effect of adsorbent dose

Figure 5 shows the effect of different adsorbent doses of magnetic beads on the adsorption of MB and MO at the optimum pH observed in the previous section. From the results we observe that the use of 2.5 grams of beads is sufficient to reach the highest %ADS of MB. Utilizing more adsorbent does not cause any considerable increase in the adsorption. This could be understood as the saturation of the adsorbent surface under these experimental conditions. Rubin *et al.* [11] studied the adsorption of phenolic compounds on brown algae, observing that 0.5 grams of the alga leveled off the adsorption percentage. They considered that the plateau observed in the adsorption at high biomass concentration is a consequence of partial aggregation of the algae in solution that reduces the number of available adsorption sites. In this specific study,

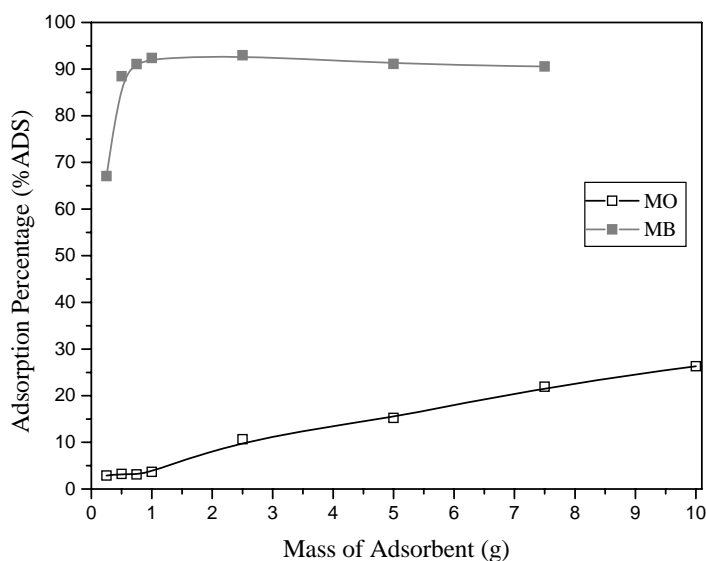


Figure 5. Effect of the adsorbent dose on MB and MO adsorption by magnetic alginate beads.

this could also apply. Due to the fact that the alginate beads are magnetized, the higher number of beads in the same solution promotes the aggregation of beads. These magnetic forces (higher concentration of magnetite) prevent the occupation of the active centers.

For MO, not more than 5 grams of magnetic alginate beads is required to saturate the surface, since an increasing adsorption causes small changes in the adsorption. This experiment was carried out based on the wet mass of the beads.

Adsorption isotherms-equilibrium state

The adsorption of a substance from one phase to the surface of another in a specific system leads to a thermodynamically defined distribution of that substance between the phases as the system reaches the equilibrium. This distribution can be expressed in terms of adsorption isotherms [6, 14, 19]. The Langmuir equation assumes that (i) the solid phase presents a finite number of identical sites which are energetically uniform; (ii) there is no interaction between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption; and (iii) a monolayer is formed when the solid surfaces reaches the saturation. While the Langmuir isotherm assumes that enthalpy (energy released or absorbed) of adsorption does not depend on the amount adsorbed, the Freundlich isotherm is derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in

the fraction of occupied sites and based on sorption on heterogeneous surfaces. On the other hand, Dubinin and Radushkevich in 1947 developed the D-R isotherm in accounting for the effect of porous structure of an adsorbent.

All these isotherms can be mathematically described and their constants can be determined according to Equations (3), (4), and (5):

Langmuir model

$$q = \frac{q_{\max} b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (3)$$

where q_{\max} is the maximum adsorption capacity under these working conditions, b is a constant related to the affinity between adsorbent and dye.

Freundlich model

$$q = k C_{\text{eq}}^{(1/n)} \quad (4)$$

where k and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Dubinin-Radushkevich (D-R) model

$$q = q_{\max} \exp(-B\varepsilon^2) \quad (5)$$

where B is the activity coefficient related to the Mean Adsorption Energy (mol^2/J^2) and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_{\text{eq}})$). The Mean Adsorption Energy, E (kJ/mol) can be calculated with the equation: $E = (2B)^{-1/2}$.

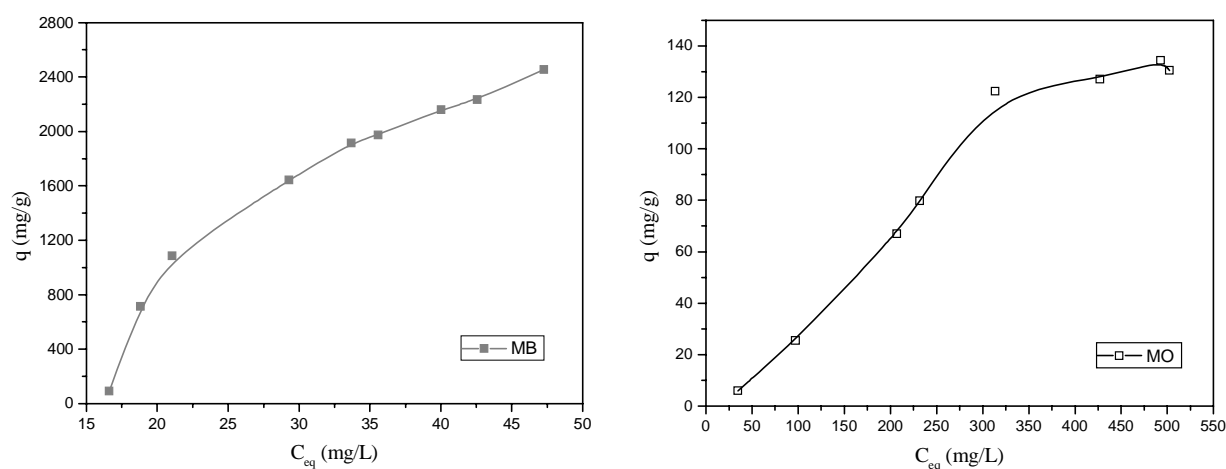


Figure 6. Adsorption isotherm of MB (left) and MO (right) on magnetic alginate beads.

Both isotherms are given in Figure 6, whereas Table 1 presents the correspondent constants along with the coefficients of linear correlation (R^2) associated with each linearized model. As we can observe in Table 1, the maximum value for the adsorption capacity for MB was $q_{\max} = 10,851.64$ mg of MB per gram of adsorbent. However, the q_{\max} , according to the Langmuir theory, for MO is 58,411.21 mg/g. The explanation for this discrepancy could be the solubility and the polarity of MO. MO is a molecule that is very compatible with alginate; in theory the adsorption capacity of MO could be higher than MB. However, its poor solubility in water limits the adsorption. MO is only soluble at a pH higher than 4. By looking at Figure 3, the adsorption of MO exponentially increases from pH 5 to 4. This is an indication that at even lower pH values (around 2) the adsorption of MO would be much higher than MB. This process is just not seen due to low solubility of MO.

It can be hypothesized that the reason why MO could have more affinity towards alginate is due to the polarity of the molecule. The sulfonic group is extremely polar, compared to the tertiary amines that are present in MB. This polarity would enhance the attraction between the hydroxyl groups and the sulfonic acids via hydrogen bonds or other polar interactions. Unfortunately, this interaction cannot be seen because the rest of the molecule of

MO is very non polar and precipitates out of the solution before this interaction could happen. Therefore, under the experimental conditions, alginate beads adsorb MB better than MO. This is corroborated by the affinity Langmuir constant “b” of 161.364 for MB compared to the 8.3×10^{-4} for MO.

The Freundlich theory also shows a better adsorption capacity for MB as indicated by the k constant. The higher adsorption intensity, represented by the “n” Freundlich constant also demonstrates the better affinity between alginates and MB, in a similar way to the “b” Langmuir constant. Lastly, the importance of the D-R model resides on the Mean Energy of Adsorption that can be determined from the B constant. The results show that for MB, the Mean Adsorption Energy is around 77 J/mol whereas for MO is 3 J/mol. These indicators confirm that under experimental conditions, MB has stronger interactions with alginate than MO. It is important to highlight the fact that both dyes were fitted to all the Adsorption models with very high correlation coefficients, meaning that their adsorption is actually a mixture of the three mechanisms. On the other hand, studies with fungus [20] and other adsorbents [21] reported much lower adsorption capacity towards the dye RR198 with a $q_{\max} = 83.66$ mg/g. This demonstrates the applicability of these adsorbents compared to other cheap adsorbents.

Table 1. Parameter and constants for the adsorption isotherms of MB and MO on magnetic alginate beads.

Adsorption Isotherm	Methylene Blue (MB)	Methyl Orange (MO)
Langmuir		
q_{\max} (mg.g ⁻¹)	10851.64	58411.21
b (L.mg ⁻¹)	161.364	8.3×10^{-4}
R^2	0.989	0.909
Freundlich		
k (L.g ⁻¹)	111.508	8.5451
N	1.2463	0.78474
R^2	0.989	0.987
Dubinin-Radushkevich		
q_{\max} (mg.g ⁻¹)	2975.59	18872.1
B x 10 ⁻⁴ (mol ² .J ⁻²)	0.8305	30.74
R^2	0.989	0.965

Effect of salinity

The adsorption capacity is connected with several types of electrostatic interactions, as demonstrated with the effect of the initial pH. These electrostatic interactions include complexation, ionic exchange, and electrostatic interactions; between the adsorbate and adsorbent. They strongly depend on the electrostatic environment of the solution that can define the existence or non existence of the interaction [22]. The presence of ions in solution represents strong competitors for the active sites on the adsorbent. Figure 7 shows the effect of salinity on the adsorption of both dyes. From the results we can conclude that MB adsorption is diminished in presence of salt, whereas MO adsorption undergoes an initial increment followed by a negative effect at higher salt concentrations. This weird behavior of MO in the presence of salt could be understood as the shielding of the negative charges at 0.25 M salt. Sodium ions would work as spacers between the alginate and the sulfonate ions enhancing their attraction. This effect seemed to be reversed at 0.5 M salt, maybe due to the higher population of the counter ions (nitrate) which were not relevant at lower concentration. Salinity does not have the same effect on MB because in that case sodium ions directly compete for the alginate adsorption sites. From the Figure 7, it can be concluded that at 0.25 M salt concentration, the adsorption of MB decreased to 83%, whereas MO adsorption in 0.25 M salt increased by more than 50%. It is

strongly suggested to carry out more studies of salinity on MO to enhance its adsorption.

Desorption experiments

The recycling of the adsorbent in consecutive rounds is the goal of an environment friendly adsorbent. It would be disadvantageous to synthesize new adsorbent every time we decontaminate a water source and then discard it. In order to complete this, 20 mL of cosolvents of different chemical nature were added to dye-loaded beads and shaken for 4 hours. The cosolvents were selected based on their polarity, capacity of formation of hydrogen bonds, acidity, basicity and salinity. The results are shown in Figure 8. The data is in complete agreement with the previous results of pH, mass, salt and isotherms. MB is recovered at almost 100% by using hydrochloric acid (HCl). This is completely understandable due to the neutralization of the alginate. As concluded before, the negative charge of the alginate interacts with the positive charge of MB. Once the alginate loses its charge, the affinity towards the dye decreases dramatically. MB is also efficiently desorbed in NaCl, most likely due to competition of sodium ions with the alginate active sites.

As for MO, the low affinity dye/alginate makes this interaction very weak and easy to break by any cosolvents. The most efficient resulted to be acetone. This might be due to its amphipathicity, being able to dissolve apolar or not very polar

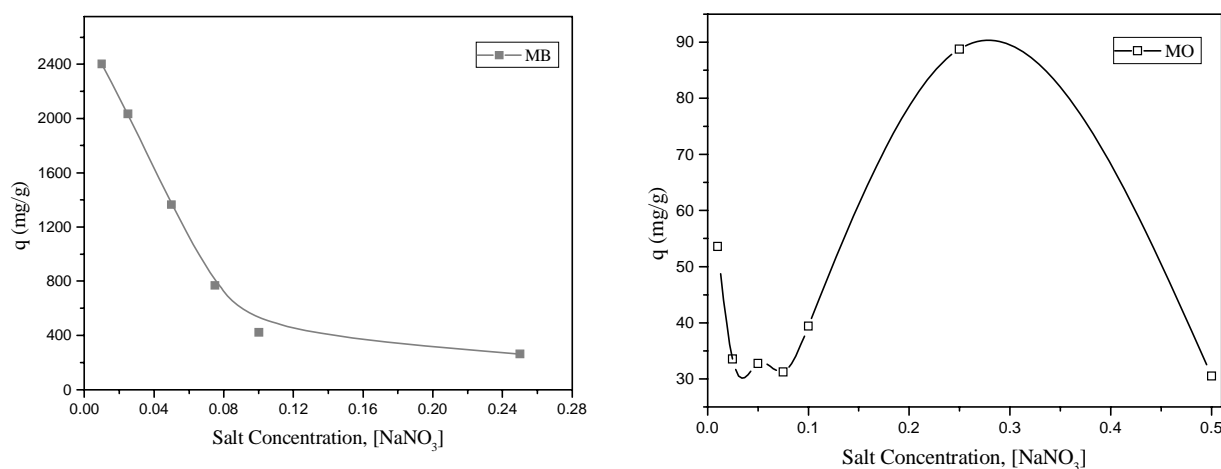


Figure 7. Effect of the ionic strength on the adsorption of MB (left) and MO (right) on magnetic alginate beads.

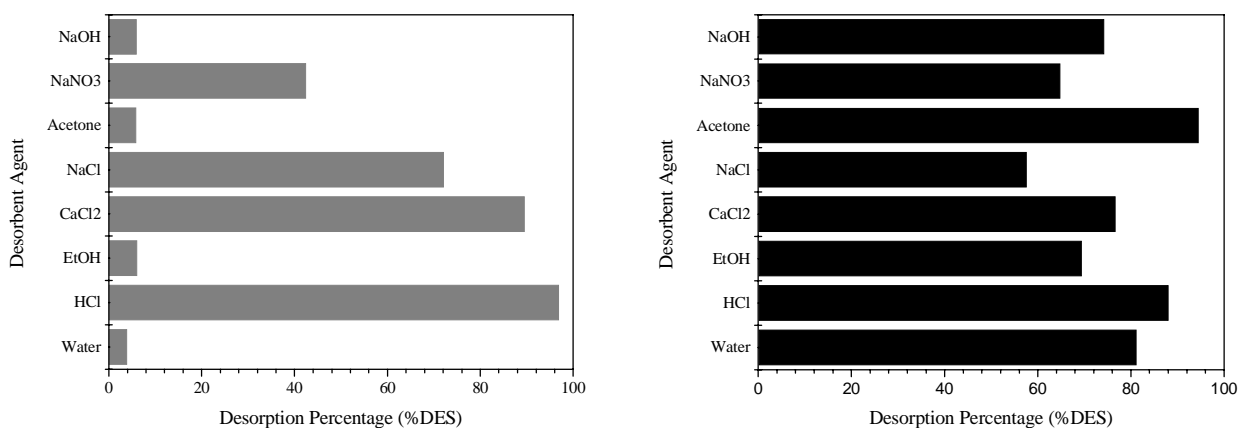


Figure 8. Desorption of MB (left) and MO (right) in different cosolvents.

molecules like MO. It is very interesting that CaCl_2 is a very decent desorber in both cases; we believe that the stabilizing formation of the egg box structure favors the replacement of any ion or molecule by calcium (II) ions [23].

CONCLUSIONS

This work shows that magnetic alginate beads can potentially be utilized as adsorbents for Methylene Blue (MB) and Methyl Orange (MO). The magnetic particles were encapsulated in alginate gel beads to facilitate their removal from the solution by using a conventional magnet and avoid the use of other techniques such as centrifugation or filtration. Batch experiments were conducted at room temperature to evaluate the effect of initial pH solution, mass of adsorbent, isotherms, salinity and desorption. The pH showed a strong effect on the adsorption of both dyes, elucidating a mostly electrostatic adsorption mechanism. The optimum pH values were 7 and 4 for MB and MO, respectively. These results were in complete agreement with the acid/base properties of alginate and dyes. The adsorbent dose effect was also studied and indicates that 2.5 and 5 g of wet adsorbents are needed to reach equilibrium for the adsorption of MB and MO. The addition of extra adsorbent did not affect the equilibrium due to saturation of the adsorbent's surface. It was suggested that the magnetic particles are responsible for the low adsorption at high adsorbent doses, due to the attractive magnetic field in a large volume.

The magnetic attraction reduces the contact surface between dyes and alginate, causing a lower adsorption. The process was fitted to the mathematical models of Langmuir, Freundlich and Dubinin-Radushkevich with very high correlation coefficients. This reflects the presence of the three mechanisms. According to Langmuir theory, the maximum adsorption capacities were 10,851.64 and 58,411.21 mg of dye/g of beads for MB and MO, respectively. The calculated parameters from the isotherms demonstrate an interesting affinity between adsorbate and adsorbent. Salinity reported a controversial result on MB and MO. As expected, the addition of more salt decreased the adsorption of MB due to the competition with sodium ions for the alginate's active sites. However, MO showed an increasing adsorption at 0.25 M NaNO_3 ; this could be attributed to the shielding of the negative charges that repel each other. Sodium ions would work as a barrier between the negative charge of MO and alginate, making possible the adsorption interaction. Finally, desorption experiments corroborated the driving adsorption mechanisms. MB is better eluted with HCl due to protonation of alginates that causes the reduction of electrostatic interactions with MB. On the other hand, MO is better desorbed with acetone due to its more non polar properties and the ability to dissolve MO. Even though CaCl_2 was not the strongest desorbent, it was very effective for both dyes. This indicates the strong egg box structure in alginates and capacity to displace any ion or molecule.

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