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Entrapped Zinc Oxide and Titania Nanoparticles in Calcium Alginate Beads for the Removal of Methylene Blue (MB): Adsorption Properties and Photocatalytic Stability

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In this work, zinc oxide (ZnO) and titania (TiO_2) nanoparticles were entrapped in calcium alginate (Ca-Alg) beads to form a composite photocatalytic adsorbent material. The adsorption and photocatalytic properties of ZnO and TiO_2 Ca-Alg beads were investigated for different amount of encapsulated nanoparticles. In particular, 2% w/w, 5% w/w, 7% w/w of ZnO and 2% w/w, 5% w/w, 10% w/w of TiO_2 calcium alginate beads were synthetized and Methylene Blue (MB) was selected as target pollutant. Adsorption batch test revealed the existence of a maximum removal percentage of MB (at equilibrium conditions) according to the nanoparticles concentration: 54% and 40% of MB removal was obtained for 2% w/w of ZnO and 5% w/w of TiO_2 respectively. Moreover, it was also observed that the kinetic of the process improves increasing the amount of nanoparticles in the beads. The pseudo-first-order kinetic model was used for fitting and it reproduces very well the behavior of experimental data. Photocatalytic batch tests revealed that, in the range of time analysed, negligible photocatalytic activity was recorded for ZnO Ca-Alg beads, while an intense photocatalytic activity was observed for TiO_2 Ca-Alg beads. In the latter case the stability of the alginate structure was compromised as detected by a spectrophotometric analysis.

1. Introduction

Clean water is an essential resource for human health, agriculture, energy production, transport and nature. But it is also under multiple pressures that compromise its quality. Human, agricultural and industrial activities alter water quality becoming polluted by organic and inorganic compounds some of which are very persistent and dangerous such as pathogens, fertilizers, pesticides, personal care products, and heavy metals (Zandaryaa and Mateo-Sagasta, 2018). Among various available water treatment technologies, adsorption process is one of the most used because of ease of operation and simplicity of design (Faust et al., 1987). Moreover, this process is flexible toward the removal of different types of pollutants.
Thanks to their high specific surface area, nanoparticles have been successfully adopted as adsorbent material in particular for the removal of heavy metals (Bavasso et al., 2018) (Bavasso et al., 2019) and dyes (Anastopoulos et al., 2018). As regarding the removal of a model compound as Methylene blue (MB) from wastewater, in literature are available experimental results obtained with magnetite (Fe_3O_4) nanoparticles (Khan et al., 2019), zinc oxide (ZnO) nanoparticles (Zhang et al., 2013) and titania (TiO_2) nanoparticles (Fetterolf et al., 2003) thus highlighting the excellent adsorption properties of such materials. Furthermore, nanoparticles as ZnO and TiO_2 are known to have photocatalytic properties which may lead to the complete degradation of target pollutants with the occurrence of radical species formation (Zhang et al., 2012). However, there are some drawbacks related to nanoparticles adoption in large scale applications for example the release of nanoparticle in water solutions because the difficulty of separation and, in case of column operations, the extremely high packing factor due to the nanoscale dimensions of the particles. To avoid those issues, the entrapment of nanoparticles in calcium alginate beads was investigated.

Calcium alginate hydrogel is synthesized from alginic acid salt, an inexpensive and easily available natural biomaterial obtained from algae. Due to its biocompatibility and stability, calcium alginate has been widely used to encapsulate enzymes (Kierstan and Buke, 1977), proteins (Chaudhari et al., 2015), drugs and adsorbent materials (Wang et al., 2019).
Despite many works were conducted to investigate the effectiveness of nanoparticles entrapped in calcium alginate beads for the removal of pollutants from aqueous solutions, to the best of our knowledge, none of them was focused on the influence of nanoparticle loading in the beads on the kinetics of the adsorption process which is of crucial importance for future scale up of the technology. Bilici et al., (2019) produced alginate beads with different percentages (5% w/w, 7.5% w/w, 10% w/w, 15% w/w) of magnetite and zinc oxide alone or in compresence, but adsorption process was studied for beads containing about 15% w/w of nanoparticles without evaluating the effect of nanoparticle load on adsorption kinetic. Kanakaraju et al., (2017) entrapped TiO_2 and ZnO together in alginate beads and studied the adsorption of Cu(II) at different ratios of the two nanoparticles maintaining constant the total nanoparticle loading in the beads. Other works were more focused to detect a suitable adsorbent for specific compounds testing calcium alginate beads with a fixed amount of nanoparticles concentration, i.e. magnetic calcium alginate beads were successfully used to adsorb Pb(II) (Bée et al., 2011) or Cu(II) (Germanos et al., 2020).
In this work the impact of ZnO and TiO_2 loading in calcium alginate beads on the kinetic of adsorption of Methylene Blue (MB) was investigated. Moreover, considerations about the kinetic of photocatalysis and stability of the alginate beads during the exposure on UV light source are provided.

2. Materials and methods

2.1 Chemicals

Alginic acid sodium salt powder (Sigma-Aldrich) and calcium chloride anhydrous, $CaCl_2$ (Sigma-Aldrich) were used to prepare the calcium alginate beads. Commercial titanium dioxide and zinc oxide nanoparticles (Sigma-Aldrich) were used for the preparation of decorated beads. Their activity as adsorption capacity and photocatalytic reactivity were evaluated by monitoring the removal of Methylene blue ($C_{16}H_{18}ClN_3S$, MB; Sigma-Aldrich).

2.2 Alginate beads synthesis

The alginate beads used in this work were synthesized in three steps:

1. Addition of different quantities of metal oxides (TiO_2 and ZnO) to 50 mL of demineralized water little by little and under constant stirring, thus forming a homogeneous suspension of white color. In particular, for TiO_2 1g, 2.5 g, 5g were added in order to have the following percentage in weight respect to the water solution 2%, 5%, 10%; for ZnO 1g, 2.5 g, 3.5 g were added in order to have the following percentage in weight respect to the water solution 2%, 5%, 7%.
2. Addition 0.75 g of sodium alginate (1.5% w/w) to the suspension under constant stirring and heating to prevent the formation of lumps.
3. Extrusion with a syringe of the alginate solution into 100 mL 1% w/w $CaCl_2$ aqueous solution.

The concentration of sodium alginate and $CaCl_2$ were chosen according to the work of Cuadros et al., (2012), to promote the minimum crosslinking density and to facilitate the intra particle diffusion.

2.3 Kinetic tests

A solution of 50 mL with a concentration of 10 mg/L of MB and kept, under constant stirring, at the fixed temperature of 293 K, was used to perform all the kinetic tests. Alginate beads concentration in the solution was calculated in order to have always the same alginate to liquid ratio of 5.5:100. According to this ratio, the amount of nanoparticles entrapped in the calcium alginate beads was different for each test. For simplicity, the percentage in weight of TiO_2 and ZnO in the beads was referred to the one of the liquid alginate solution obtained in the first step of the alginate beads synthesis (see previous section) which is of 2%, 5%, 10% for TiO_2 and 2%, 5%, 7% for ZnO. Adsorption and photocatalytic tests were performed in series: the adsorption test lasted till the equilibrium conditions (obtained after 120 min) were reached; after that, photocatalysis was activated by exposing the solution to UV light (365 nm and $irradiance_{max}$= 20 W/m^2).
The concentration of MB removed was measured by spectrophotometric analysis using a PG Instruments (United States) T80+ UV/Vis spectrophotometer (with glass cells of 1 cm path length) at λ = 664 nm. The percentage of MB removed (R%) during the test was calculated with the following equation:

$$R(\%) = \frac{C_0 - C(t)}{C_0} \cdot 100 \quad (1)$$

Where C_0 (mg/L) is the concentration of MB at the beginning of the test and C(t) (mg/L) is the concentration of MB calculated at time t.

3. Results and discussion

3.1 Adsorption kinetic tests

Adsorption kinetic tests were carried out to evaluate the influence of nanoparticle loading into calcium alginate beads towards the adsorption performances of the composite material. In Figure 1 is reported the ratio between the liquid concentration of MB during time respect to its initial concentration (C/C_0) for different content of ZnO (Figure 1a) and TiO_2 (Figure 1b) in the alginate beads.

The addition of nanoparticles strongly influenced the adsorption process of MB removal with both the adopted nanoparticles. In particular, a maximum removal of MB was obtained with a ZnO dosage of 2% that can be considered as an optimal value (Figure1a). A further increase in the dosage of nanoparticles resulted in a decrease of the removal of the dye. Similar trends were observed when TiO_2 was adopted as nanoparticle filler (Figure 1b) reaching a maximum MB removal using a nanoparticle content of 5%. Also in this case a further addition proved to be ineffective on the MB removal. This effect can be explained by considering that with the increasing on nanoparticles concentration an higher specific surface area is available for adsorption in the mesoporous structure of the calcium alginate hydrogel (Hassan et al., 2014), but, at a certain concentration, the nanoparticles packing starts to become so high that some active sites are no longer accessible to the target compound creating a “screening effect”.

The pseudo-first order model was used to describe the kinetic of the process and the equation used was made explicit respect to the concentration in the liquid solution as follows:

$$\frac{C(t)}{C_0} = \frac{C_e}{C_0}(1 - e^{-kt}) + e^{-kt} \quad (2)$$

where C_e (mg/L) is the concentration of MB at equilibrium conditions (calculated at120 min) and k (min^{-1}) is the pseudo-first-order rate constant of the kinetic model. A non-linear regression was performed to fit the experimental data with Eq(2) using as objective function the minimization of the mean square error

$$\emptyset = min\left[\frac{1}{N}\sum_{i=1}^{N}\varepsilon_i^2\right] \quad (3)$$

where N is the number of experimental points and ε_i is the error calculated by the difference of the experimental data and the values predicted by the model. As it is observed in Figure 1, in both cases the pseudo first order model describes perfectly the kinetic behavior of the system. Moreover, it is possible to detect that, depending on nanoparticle loading, the speed of the process is also influenced.

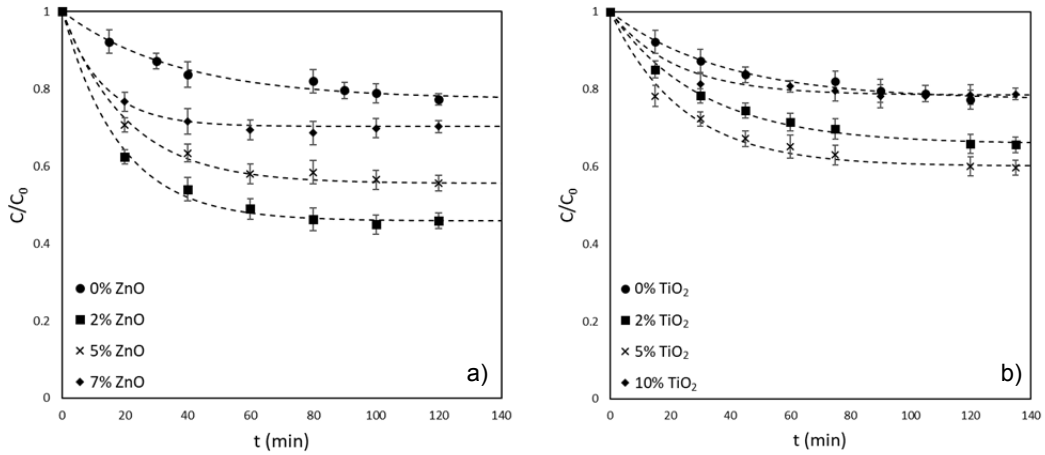

Figure 1: MB adsorption data fitting with the pseudo first order kinetic model for ZnO (a) and TiO_2 (b) calcium alginate beads.

In Figure 2, the removal percentage of MB calculated at equilibrium conditions (R_e) using Eq (1) and the value obtained from fitting of the pseudo-first-order rate constant k, are plotted versus nanoparticles concentration. In particular, Figure 2a and Figure 2b refer to ZnO decorated beads and TiO_2 decorated beads, respectively. The first important evidence is the existence of a maximum removal percentage of MB at equilibrium in the investigated range of nanoparticle loading. In particular, in the case of zinc oxide nanoparticles, such maximum was detected around the 2% ZnO corresponding to a MB removal of 54%, while for titania the maximum was detected around 5% TiO_2 corresponding to a MB removal of 40%.
The second important evidence is that an enhancement on kinetic process was observed with the increasing of nanoparticle loading. In fact, the highest pseudo-first-order rate constant k was calculated in case of the highest nanoparticle concentration in the alginate beads. This effect could be attributed to a greater availability of active sites on the beads surface which enhances the mass transfer driving force and thus the kinetic of the process.
As a general comment, it was pointed out that, between the two types of nanoparticles used, ZnO shows a higher affinity respect to TiO_2 toward MB adsorption. This result was confirmed by comparing the results obtained by Zhang et al., (2013) and Fetterolf et al., (2003).

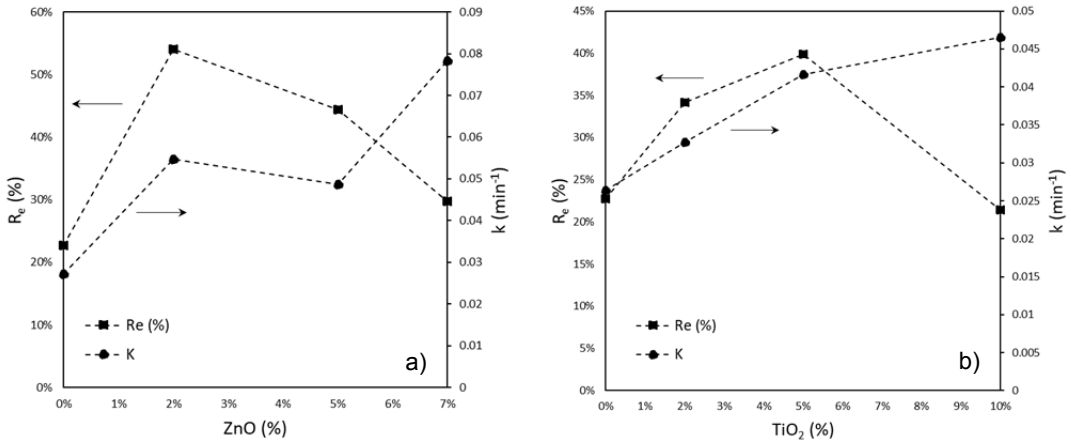

Figure 2: Plot of the removal amount of MB at equilibrium (R_e) and the pseudo-first-order rate constant (k) respect ZnO (a) and TiO_2 (b) percentage in calcium alginate beads.

3.2 Photocatalysis and stability

Photocatalytic tests were conducted to evaluate the attitude of decorated beads to MB removal and mineralization under an UV light source. Lam et al., (2017) already pointed out that calcium alginate beads degrade after a long time (more than 20 h) exposition under UV light as a consequence of radical species formation that promotes the matrix degradation. In this work, since the exposure time was maintained for 2 h, such behavior was not detected. Moreover, for the investigated range of time under UV light (40 min), ZnO calcium alginate beads showed a not significant photocatalytic activity (data not reported) thus suggesting a possible interference of the alginate matrix on ZnO photocatalytic properties. The stability of the alginate beads was evaluated when the maximum nanoparticle load was adopted (10% TiO_2) to determine the capability of the matrix to resist the attack of radical species where their formation is promoted by the availability of photoreactive materials.
As shown in Figure 3, when light is not provided, MB is adsorbed by the 10% TiO_2 beads till equilibrium conditions were reached. Once switched on the UV lamp (at 130 min), an immediate decrease of MB was recorded (Figure 3a) confirming the degradation of MB attributable to radical species formation thanks to the well-known photocatalytic activity of nanoparticles (Chin et al., 2010). As regards to the stability of alginate beads, during photocatalytic tests, a modification of MB spectrum was observed in the wavelengths range of 500 – 600 nm (Figure 3b). Although there was a reduction in the characteristic peak of MB, the increase recorded in the low wavelengths range was associated with the progressive release of nanoparticles in the aqueous solution. This effect was already observed by Lam et al., (2017) and confirms that dispersed nanoparticles in water solution may influence the absorbance of the solution itself. Therefore, it is possible to affirm that alginate beads are not suitable carriers for photocatalytic nanoparticles since they lack of stability during the photocatalytic activity.

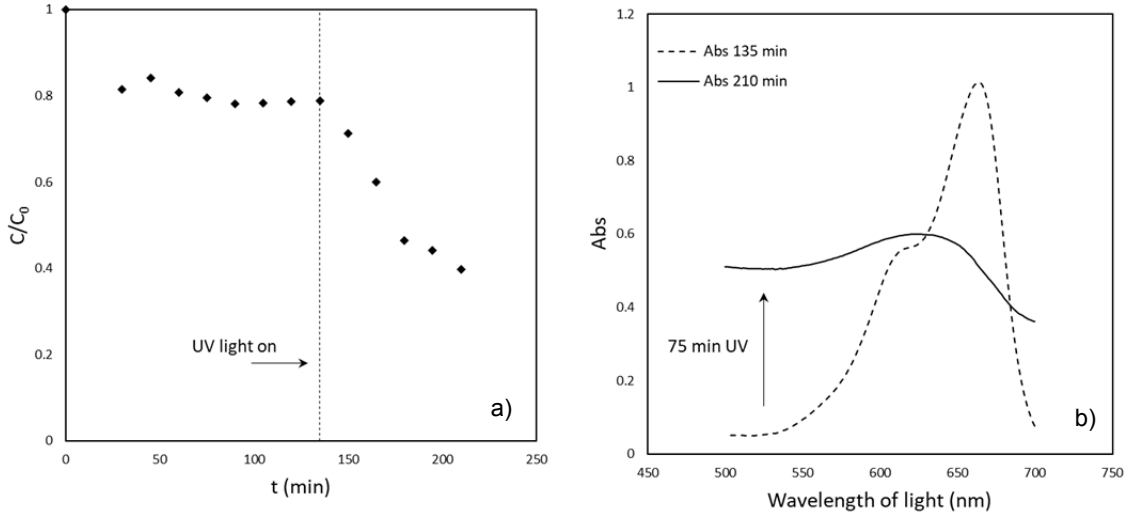

Figure 3: Adsorption and photocatalytic batch test for 10 % w/w TiO_2 calcium alginate beads nanoparticles. Concentration decrease versus time before and after UV light exposure (switched on after 135 min) (a); MB spectrum of the liquid solution at 135 min (just before UV light exposure) and 210 min (after 75 min under UV light) (b).

4. Conclusions

The aim of this work was to evaluate the effect of nanoparticles concentration in calcium alginate beads toward adsorption capacity and kinetics. According to the results of batch experiments, it was observed that the presence of ZnO and TiO_2 strongly influence the adsorption performances of calcium alginate beads. In particular, it is possible to conclude that exist a percentage of entrapped nanoparticles which maximizes the amount of removed MB at equilibrium (2% for ZnO and 5% forTiO_2). Moreover, the adsorption kinetic prove to follow a pseudo first order kinetic model and that it is promoted for high nanoparticles concentrations. A better understanding of the kinetics of the process, is crucial to design a continuous column system.

Among all these considerations, it was also confirmed that ZnO has a higher affinity toward the adsorption of MB respect to TiO_2. After exposition of the beads under UV light, it was confirmed, as reported in literature, that calcium alginate beads degrade during photocatalytic activity. This effect has to be taken into account in case of regeneration of alginate beads when photocatalytic nanoparticles are used for the decoration of such materials. Further experiments are necessary to evaluate if, in case of using ZnO nanoparticles, it is possible to modify the beads matrix to solve the stability without modifying its adsorption capacity. Further studies are also necessary to evaluate the suitability of applying hydrogel spheres for real wastewater treatment operations.

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