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Pilot Batch-Scale Reactor for Glyphosate Removal Using Hybrid Magnetic Graphene

Julio C. Santos[a], Jean C. A. Sousa[a], Ana C. S. Almeida[a], Natália C. Homem[c], Rosângela Bergamasco[c], Francielle Gasparotto[a,b], Luciana C. S. H. Rezende[a,b], Natália U. Yamaguchi[a,b*]

[a]Centro Universitário de Maringá – Unicesumar, Maringá, Paraná Brazil.
[b]Instituto Cesumar de Ciência, Tecnologia e Inovação – ICETI, Maringá, Paraná, Brazil.
[c]Department of Chemical Engineering, Universidade Estadual de Maringá, Maringá, Paraná, Brazil.
natalia.yamaguchi@unicesumar.edu.br

In this study, magnetic manganese ferrite microspeheres have been successfully synthesized on graphene nanosheets using an one-pot solvothermal method. It was reported 80% of glyphosate removal from aqueous solution using the hybrid magnetic graphene material, $MnFe_2O_4$-G, in a pilot batch-scale reactor. The adsorbent was regenerated with 0.1 mol L^{-1} NaOH solution in the batch reactor, showing to be a reusable adsorbent. The results showed that the pilot batch reactor using $MnFe_2O_4$-G could be used as an alternative to water treatment contaminated with glyphosate.

1. Introduction

Glyphosate [N-(phosphonomethyl)glycine] is used worldwide, applied as an herbicide in both agricultural and non-agricultural areas (Khoury et al., 2010). Due to the enormous quantities of glyphosate used worldwide, the concerns of its impacts on the environment and in human safety has increased, since runoff and improper disposal can lead to soil, groundwater and surface water contamination (Jia et al., 2011).

Various processes have been proposed to treat glyphosate in wastewater, but adsorption technology is a promising technique, as it is relatively easy to operate, efficient, flexible and does not form any by-products (Ghaedi et al., 2014). Various adsorbents have been tested on the removal of pesticides pollutants (Cui et al., 2012; Hu et al., 2011; Herath et al., 2016). However, there is an continuing search for more efficient and robust adsorbents for the removal of pesticides.

The successful application of adsorption process largely depends on the adsorbent. Among the adsorbent materials, graphene oxide, a two-dimensional nano-material, is an oxidized form of graphene, which is known as an emerging and new fascinating carbon nanomaterial. Graphene oxide has gained great interest as an nanosorbent for pollution control applications in recent years due to its mechanical, electrical, thermal and optical properties (Lee et al., 2015).

Functionalizing graphene to obtain graphene with specific contaminants capacities and to achieve higher removals capacities is usual practice (Maria Sarno, 2014; Casa et al., 2016; Lee et al., 2015). Graphene is an excellent adsorbent for many pollutants, but its separation from water after process treatment is still a challenge (Kumar et al., 2014). To overcome this issue, an innovative technology that has gained much attention is the use of magnetic materials. Several efforts to integrate graphene and magnetic nanoparticles have been pursued, since the new hybrid is also likely to possess enhanced functionalities with respect to adsorption. A widely range of magnetic adsorbents are investigated for the removal of different types of pollutants from water (Zhang et al., 2011; Wang et al., 2011). They offer a significant advantage over other adsorbents, which is the ability to separate them from an aqueous solution on application of a magnetic field, but still exists several gaps that are not being studied, as the evaluation of the feasibility on a pilot scale to be implemented in an industrial scale (Yamaguchi et al., 2017).

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Few studies are found in the literature using batch or continuous systems for water treatment. Graphene is still considered a recent technology for water treatment and more research for its applicability in industrial scale is needed.

Yang et al. (2015) used a material of quartz sand and GO and Fe_3O_4 in a batch column for antimony (Sb) removal. They obtained promising results and concluded that the adsorbent material developed could be used for the remediation of Sb contaminated waters.

Park et al. (2016) proposed a filter filled with Fe_3O_4 functionalized with graphene and carbon nanotubes in a Couette-Taylor flow reactor for arsenic removal. They obtained enhanced results and a possible adaptation for a household filter.

In the current study a facile approach for preparing a hybrid magnetic $MnFe_2O_4$ microspheres grown on graphene layers was reported. This study was originally motivated to investigate the performance of glyphosate adsorption using $MnFe_2O_4$-G composite magnetically separable from water in a pilot-scale reactor to evaluate the viability of the implementation in an industrial scale.

2. Materials and methods

2.1 Preparation of magnetic hybrid graphene

Graphene oxide was synthesized according the modified Hummers method (Hummers and Offeman, 1958; Maliyekkal et al., 2013). Synthesis of $MnFe_2O_4$-G was based on a one-pot solvothermal method using ferric chloride and manganese chloride as starting materials reported previously (Yamaguchi et al., 2016; Yamaguchi et al., 2017). In summary, GO, $FeCl_3.6H_2O$ $MnCl_2.4H_2O$ were dispersed in ethylene glycol with ultrasonication for 3 h. Later, sodium acetate anhydrous were added, followed by stirring for 30 min. The mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. Solid black product was obtained and washed several times by deionized water and ethanol and dried in an oven at 60°C overnight. Bare $MnFe_2O_4$ nanoparticles were also synthesized by a similar approach but in the absence of GO.

2.2 Adsorbent characterization

The morphology studies were examined using a Scanning Electron Microscope JEOL 840-A and a Transmission Electron Microscope JEOL, model JEM-1230.

2.3 Pilot batch-scale reactor system

Figure 1 shows the pilot batch-scale reactor built for this study.

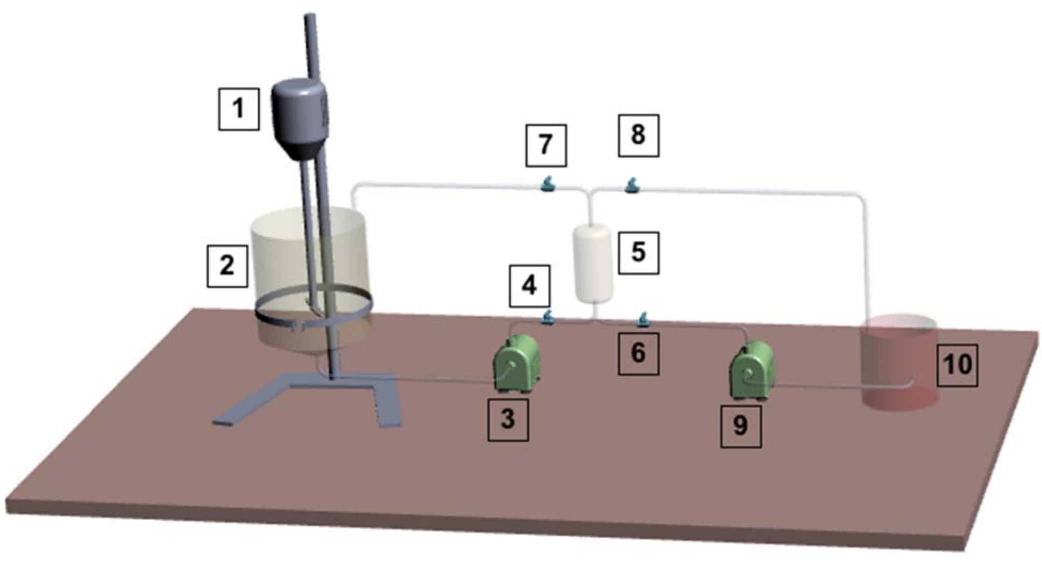

Figure 1. Scheme of pilot batch scale reactor built for this study.

The pilot batch-scale was built according to Figure 1 to verify if assays were possible to perform in a water treatment plant. Adsorption process was evaluated performing the following steps, based on a previous study (Yamaguchi et al., 2016):

Adsorption: 1 g of $MnFe_2O_4$-G was added in a tank (2) with 1 L of glyphosate 20 ppm with a mechanical agitator (1), it was stirred for 2 h.
Magnetic separation: Pump (3) was turned on and the valves (4) and (7) were opened, while in tank (5) an external magnet were placed near tank (5) to do the magnetic separation. After 2 h of magnetic separation, Pump was turned off and the valves (4) and (7) were closed. $MnFe_2O_4$-G with glyphosate adsorbed was in tank (5) and in tank (2) was treated water.
Desorption: 100 mL of NaOH 0.1 M was added in tank (10) and valves (5) and (6) were opened and pump (9) was turned on. Magnet was removed, so $MnFe_2O_4$-G was stirred and desorbed with NaOH solution for 2 h.
Magnetic separation: After 2 h a magnet was placed near tank (5) and the magnet separation was started for another 2 h.
Lavation: $MnFe_2O_4$-G was washed with distilled water and was ready to use again.

3. Results and discussion

3.1 Adsorbent characterization

Morphological structure of bare $MnFe_2O_4$ and $MnFe_2O_4$-G hybrid materials has been verified by SEM and TEM techniques as shown in Figure 2 and 3.

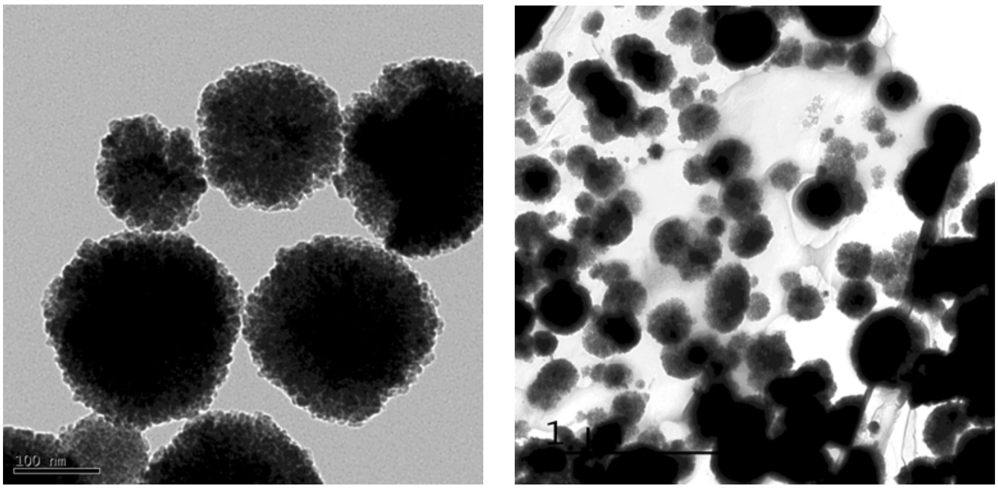

Figure 2. TEM micrograph of $MnFe_2O_4$ (a) and TEM micrograph of $MnFe_2O_4$-G (b).

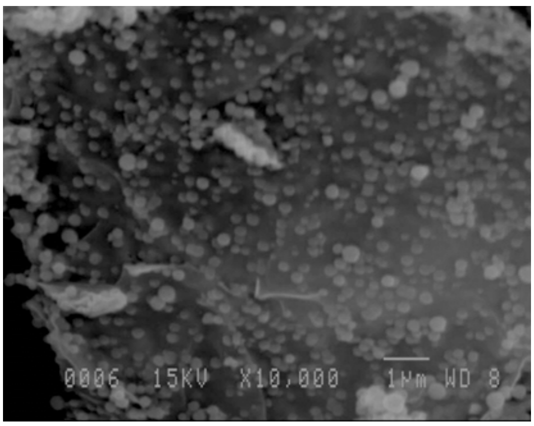

Figure 3. SEM image of $MnFe_2O_4$-G.

Microspherical particles with severe aggregation were found in Figure 2 and 3, with an average particle size ranging from 200 to 400 nm. Microspheres in $MnFe_2O_4$-G, were uniformly anchored on transparent crumpled graphene sheets (Figure 2b). $MnFe_2O_4$ microspheres were clusters, formed by the aggregation of a great number of smallers $MnFe_2O_4$ nanoparticles of 15 nm (Figure 2a). $MnFe_2O_4$ microspheres were tightly anchored on graphene surface. It is possible to confirm that, because even though after sample preparation for TEM analysis, which includes, mechanical stirring and sonication, $MnFe_2O_4$ microspheres were attached to graphene. This results suggests a strong interaction between $MnFe_2O_4$ microspheres and graphene, with an enhanced mechanical stability (Yao et al., 2012; Yamaguchi et al., 2017).

3.2 Pilot batch scale reactor system

Assays of glyphosate removal on aqueous solution were made to verify the viability of the pilot batch scale reactor system as a possible future alternative to water treatment. Initial assays were realized to determine the equilibrium time.

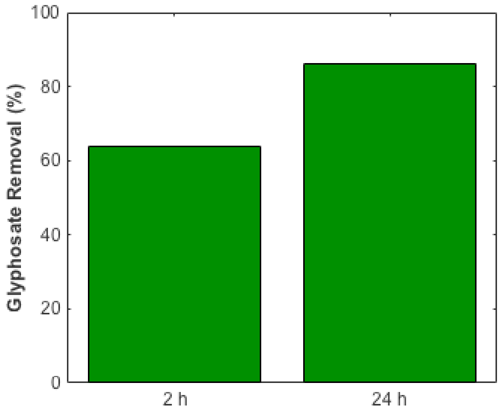

Figure 4. Glyphosate removal with time using $MnFe_2O_4$-G.

In Figure 4, $MnFe_2O_4$-G nanosorbent adsorbed glyphosate with an initial concentration of 20 mg/L. Glyphosate removal rate and adsorption capacity rapidly increase when contact time ranges from 0 to 1 h and continue increasing gradually from 1h to 6 h, showed in previous work (Yamaguchi et al., 2016), and did not showed a great difference between 2 and 24 h of adsorption time. Thus, it was chosen an equilibrium time of 4 h.

After equilibrium time was determined, cycles of adsorption-desorption were performed as described in scheme presented in Figure 1. The results of adsorption-desorption assays are shown in Figure 5.

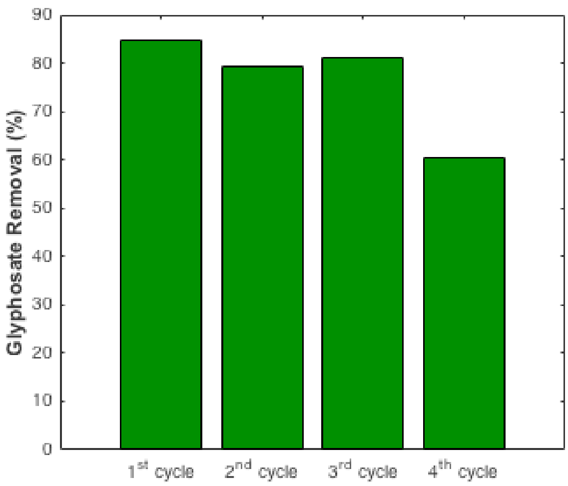

Figure 5. Results of glyphosate removal after adsorption-desorption assays.

The results showed that glyphosate desorption was 84.5% in the first cycle, followed by lower desorption rates, around 80% in second and third cycles. In the fouth cycle a great decrease in glyphosate removal happened. This result suggests that after each cycle, glyphosate desorption becomes more difficult to desorb. A possible explanation for this result is that after desorption with NaOH 0.1 M, some negative charges are left on $MnFe_2O_4$-G surface, and glyphosate molecules adsorbed becomes more difficult to desorb, because is already negative, so to desorb it should be more negative (or NaOH more concentrate), and in each desorption process it becomes more negative and less efficient (Yamaguchi et al., 2017).
Furthermore, a decrease in glyphosate removal was already expected, due $MnFe_2O_4$-G particles losses in mechanical process during separation and washing.

4. Conclusions

$MnFe_2O_4$ nanohybrid has been successfully synthesized on few layer graphene. The synthesis was confirmed by SEM and TEM micrographs. The obtained results showed that is possible to enhance the quality of polluted water with glyphosate using the hybrid magnetic graphene adsorbent with the pilot batch-scale reactor developed in the present study. Therefore, the pilot batch-scale reactor could be considered as an alternative treatment for water contaminated with glyphosate, although, further studies for continuous operation are still necessary and should be performed in continuous flow reactor systems with magnetic separation, regeneration, and recycling to ensure the viability for the hybrid magnetic graphene in water and wastewater treatment plants.

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