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Glyphosate Removal Using Reusable Ferrite Manganese Graphene

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The increasing use of pesticides in agriculture, environmental pollution became an imminent problem in modern society. Reusable materials as a sustainable technology has a broad application prospect in water treatment, and magnetic graphene materials are proposed in this study. Magnetic manganese ferrite nanoparticles have been successfully synthesized on graphene. It was reported 89% of glyphosate removal from aqueous solution after 6 h of contact time. The adsorbent showed to be a reusable adsorbent, as it could be reasonable regenerated with 0.1 M NaOH solution, obtaining removals higher than 80% after regeneration. The results showed that $MnFe_2O_4$-G might be used as an alternative adsorbent for water treatment contaminated with glyphosate.

1. Introduction

There is an increasing use of pesticides in agriculture, due the benefits they bring as crops production and hence in economy. However, pesticides are extremely hazardous to human health, and, its occurrence in environment should be prevented (Rubí-Juárez et al., 2016). Glyphosate is one of the most commonly used herbicide around the World for different crops (Khoury et al., 2010). It was believed to have low risks to humans, but studies in the last decade pointed to another direction, indicating that glyphosate can be can be carcinogenic (Myers et al., 2016). Therefore, it is an urgent subject to treat glyphosate from aqueous solution.

Current methods used to remove glyphosate from aqueous solution include adsorption, nanofiltration, advanced oxidation, oxidation technologies, electrochemical degradation, photocatalytic degradation and microbial degradation (Cui et al., 2012). Although all these methods seem potential options, adsorption is a promising technique for such contaminants, 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 on-going search for more efficient and robust adsorbents for the removal of pesticides.

Graphene is emerging as a new fascinating carbon nanomaterial, which has garnered a great deal of interest as nanosorbent precursor for pollution control applications in recent years. Graphene offers significant improvement in nanosorbent design owing to its mechanical, electrical, thermal and optical properties (Lee et al., 2015).

Many studies are functionalizing graphene to obtain graphene with specific contaminants capacities and to achieve higher removals capacities (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). Magnetic separation has come to overcome this issue; an innovative technology that has gained much attention. 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. Although, there are several gaps that are not being studied yet, as the evaluation of the desorption and reusability of the nanosorbent.

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 and desorption using $MnFe_2O_4$-G composite magnetically separable from water in a batch study.

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 facile one-pot solvothermal method using ferric chloride and manganese chloride as starting materials. In summary, 0.1 g of GO, 1 g of $FeCl_3.6H_2O$ and 0.376 g of $MnCl_2.4H_2O$ were dispersed in 30 mL of ethylene glycol with ultrasonication for 3 h. Later, 3 g of sodium acetate anhydrous were added, followed by stirring for 30 min. The mixture was then transferred into a 40 mL 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 (Cai et al., 2014; Chella et al., 2015; Yamaguchi et al., 2016).

2.2 Adsorbent characterization

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

2.3 Evaluation of the adsorption-desorption process for glyphosate removal

Figure 1 shows the scheme used to evaluate the adsorption-desorption process for glyphosate removal in this study.

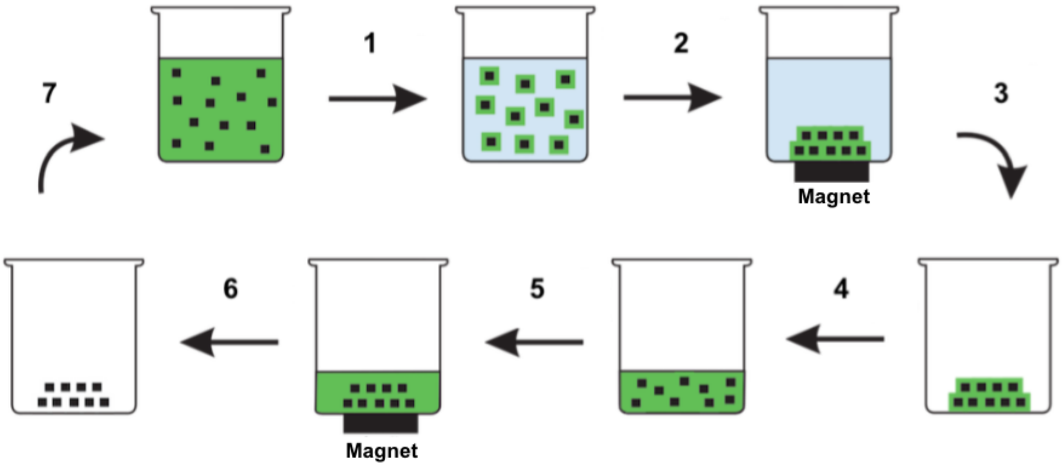

Figure 1. Scheme used to evaluate the adsorption-desorption process for glyphosate removal.

The adsorption-desorption process for glyphosate removal was evaluated performing the steps according to Figure 1. All adsorption steps were based on previous kinetics and thermodynamic studies (Yamaguchi et al., 2016). Initially 20 mg of $MnFe_2O_4$-G and 20 mL of glyphosate 20 mg/L was left in contact with agitation with 125 rpm for 24 h at 25 °C (1), than glyphosate was adsorbed and separated by an external magnet (2). The solution was collected and filtered to determine the quantity of glyphosate adsorbed by ion chromatography (3). The adsorbent was regenerated using 5 mL of NaOH 0.1 M solution during 24 h (4), and again with the aid of an external magnet, the adsorbent was separated by magnetic separation. The supernatant was filtered and collected to quantify the amount of glyphosate desorbed by chromatography analysis (5). The adsorbent was washed three times with distilled water (6) and reused to a new process of adsorption (7), until 4 complete cycles.
The desorption rate was calculated using the following equation (Xia et al., 2015):

$$R(\%) = \frac{C_1}{C_0} \times 100 \quad (1)$$

Where R is the desorption rate (%), C_1 is the glyphosate concentration in the desorption solution after desorption (mg/L), and C_0 is the glyphosate concentration calculated according to the adsorption capacity of $MnFe_2O_4$-G after desorption is completed (mg/L).

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.

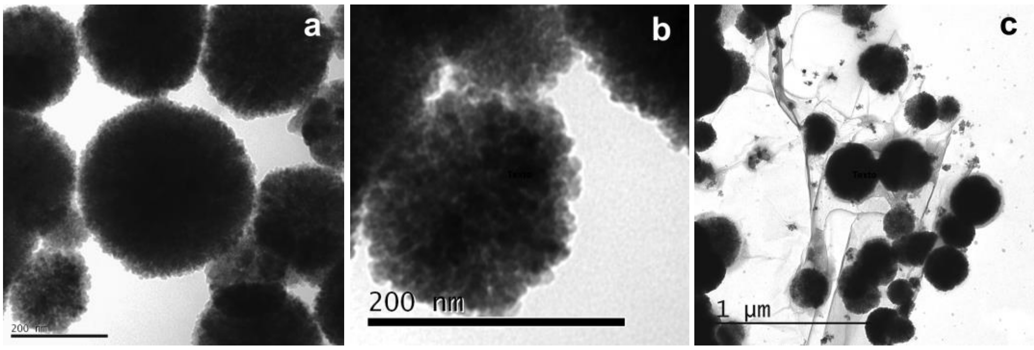

Figure 2. TEM micrograph of $MnFe_2O_4$ (a), insight from TEM micrograph of $MnFe_2O_4$ (b) and TEM micrograph of $MnFe_2O_4$-G (c).

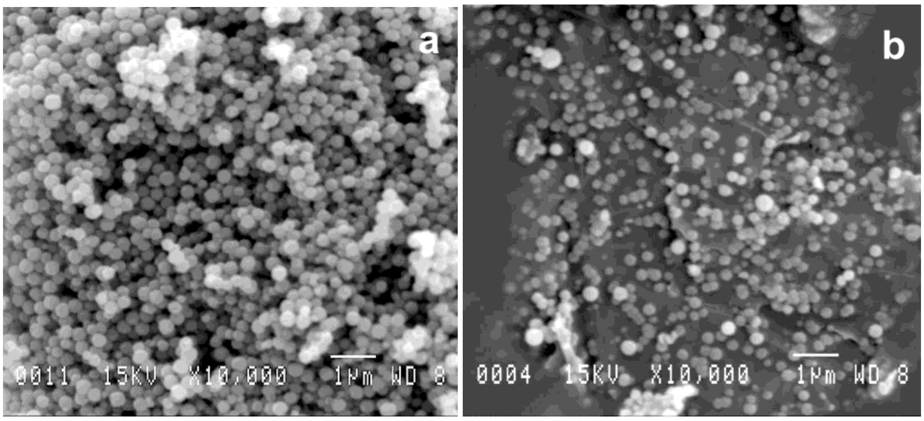

Figure 3. SEM images of $MnFe_2O_4$ (a) and $MnFe_2O_4$-G (b).

Bare $MnFe_2O_4$ presented microspherical particles with severe aggregation, with an average particle size ranging from 200 to 400 nm (Figure 3a), in contrast to the microspheres in $MnFe_2O_4$-G, which were uniformly anchored on transparent crumpled graphene sheets (Figure 2c). The $MnFe_2O_4$ microspheres were actually a cluster, formed by the aggregation of a great number of smaller $MnFe_2O_4$ nanoparticles of 15 nm (Figure 2b). The graphene structure prevented the agglomeration of the microspheres and ensured a large specific surface area due to the intimate interaction between bare $MnFe_2O_4$ microspheres and graphene sheets (Liu et al., 2013). It is noteworthy that $MnFe_2O_4$ microspheres were tightly anchored on graphene surface even after sample preparation for TEM analysis (mechanical stirring and sonication), suggesting a strong interaction between $MnFe_2O_4$ and graphene and an enhanced mechanical stability (Yao et al., 2012).

3.2 Evaluation of the adsorption-desorption process for glyphosate removal

Essays of glyphosate removal on aqueous solution were made to verify the viability of $MnFe_2O_4$-G as a reusable adsorbent for water treatment. The results for glyphosate removal are presented in Figure 4.

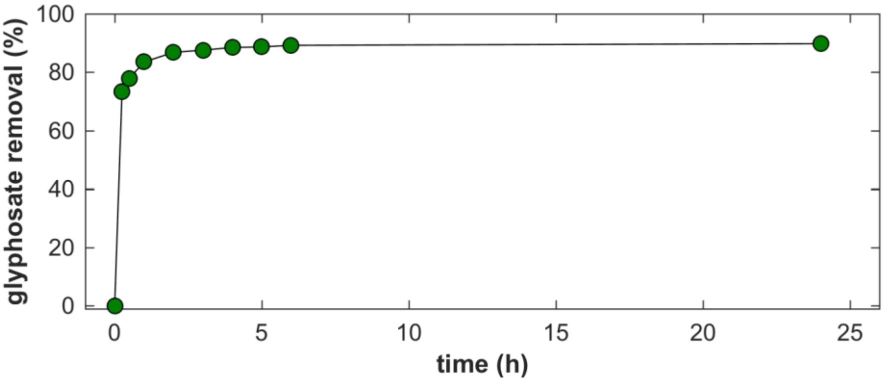

Figure 4. Glyphosate removal with time using $MnFe_2O_4$-G.

The $MnFe_2O_4$-G nanosorbent adsorbed glyphosate with an initial concentration of 20 mg/L under an optimal experimental condition. Figure 4 shows that 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. The equilibrium was achieved at 6h and the maximum removal rate was 89% after 6h.

The results of glyphosate desorption rate kinetics are presented in Figure 5. According to Figure 5, the equilibrium time of desorption was determined to be after 24 h. In 24 h, 81% of maximum desorption capacity was achieved.

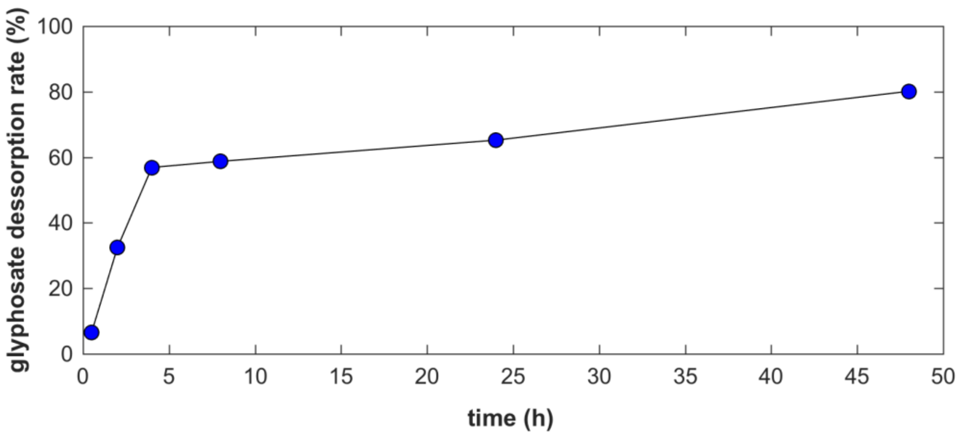

Figure 5. Glyphosate desorption rate kinetics results.

After equilibrium time was determined, cycles of adsorption-desorption were performed as described in scheme presented in Figure 1. The results of adsorption-desorption essays are shown in Figure 6.

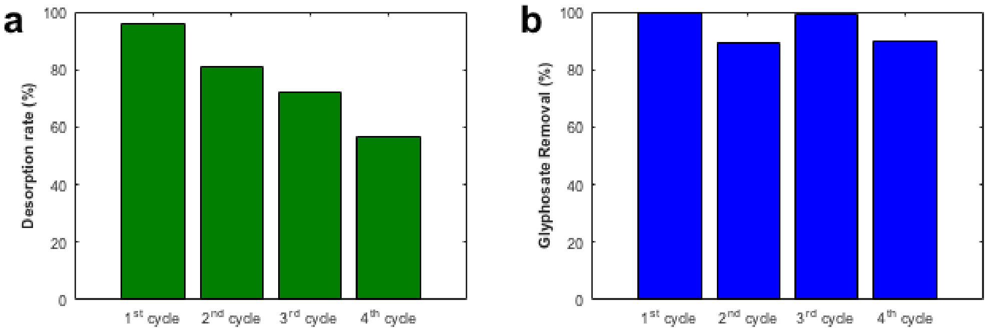

Figure 6. Results of desorption rate and glyphosate removal.

The results showed that glyphosate desorption was around 96.1% in the first cycle (Figure 6a), followed by lower desorption rates, 80.7, 72.0 and 56.4% in second, third and forth, respectively. 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. Thus, to have better results the NaOH concentration should be increased in each cycle.

In Figure 6b it was possible to verify that glyphosate removal was higher than 80% in all cycles, even though desorption rate was not complete (56 – 96%). Indicating that possibly the amount of adsorbent was in excess, obtaining a high glyphosate removal even when the desorption rate was lower. 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

The $MnFe_2O_4$-G synthesis was confirmed by SEM and TEM micrographs, and the nanohybrid has been successfully synthesized on a few layer graphene. The obtained results showed that is possible to enhance the quality of polluted water with glyphosate with 89% of efficiency using the hybrid magnetic graphene adsorbent developed in the present study after 6 h of contact time. The adsorbent also can be reasonable regenerated with 0.1 M NaOH solution showing that is a reusable adsorbent, obtaining removals higher than 80% in all cycles after regeneration. Therefore, the nanosorbent could be considered as an alternative material for treatment for water contaminated with glyphosate, although, further studies of adsorbent 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 of the hybrid magnetic graphene in water and wastewater treatment plants.

Acknowledgments

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Reference

Cai W., Lai T., Dai W., and Ye J., 2014, A facile approach to fabricate flexible all-solid-state supercapacitors based on MnFe2O4/graphene hybrids, Journal of Power Sources, 255, 170-178.

Casa M., Sarno M., Cirillo C., and Ciambelli P., 2016, Reduced Graphene Oxide-Based Siver Nanoparticle-Containing Natural Hydrogel as Highly Efficient Catalysts for Nitrile Wastewater Treatment, Chemical Engineering Transactions, 476, 307-313, DOI: 10.3303/CET1647052

Chella S., Kollu P., Komarala E.V.P.R., Doshi S., Saranya M., Felix S., Ramachandran R., Saravanan P., Koneru V.L., Venugopal V., Jeong S.K., and Nirmala Grace A., 2015, Solvothermal synthesis of MnFe2O4-graphene composite—Investigation of its adsorption and antimicrobial properties, Applied Surface Science, 327, 27-36.

Cui H., Li Q., Qian Y., Zhang Q., and Zhai J., 2012, Preparation and adsorption performance of MnO2/PAC composite towards aqueous glyphosate, Environ Technol, 33, 16-18, 2049-2056.
Ghaedi M., Ansari A., Habibi M.H., and Asghari A.R., 2014, Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: Kinetics and isotherm study, Journal of Industrial and Engineering Chemistry, 20, 1, 17-28.
Herath I., Kumarathilaka P., Al-Wabel M.I., Abduljabbar A., Ahmad M., Usman A.R.A., and Vithanage M., 2016, Mechanistic modeling of glyphosate interaction with rice husk derived engineered biochar, Microporous and Mesoporous Materials, 225280-288.
Hu Y.S., Zhao Y.Q., and Sorohan B., 2011, Removal of glyphosate from aqueous environment by adsorption using water industrial residual, Desalination, 271, 1–3, 150-156.
Hummers W.S., and Offeman R.E., 1958, Preparation of Graphitic Oxide, Journal of the American Chemical Society, 80, 6, 1339-1339.
Khoury G.A., Gehris T.C., Tribe L., Torres Sánchez R.M., and dos Santos Afonso M., 2010, Glyphosate adsorption on montmorillonite: An experimental and theoretical study of surface complexes, Applied Clay Science, 50, 2, 167-175.
Kumar S., Nair R.R., Pillai P.B., Gupta S.N., Iyengar M.A.R., and Sood A.K., 2014, Graphene Oxide–MnFe2O4 Magnetic Nanohybrids for Efficient Removal of Lead and Arsenic from Water, ACS Applied Materials & Interfaces, 6, 20, 17426-17436.
Lee X.J., Chemmangattuvalappil N., and Lee L.Y., 2015, Adsorptive Removal of Salicylic Acid from Aqueous Solutions using New Graphene-Based Nanosorbents, Chemical Engineering Transactions, 456, 1387-1393, DOI: 10.3303/CET1545232.
Liu H., Ji S., Zheng Y., Li M., and Yang H., 2013, Modified solvothermal synthesis of magnetic microspheres with multifunctional surfactant cetyltrimethyl ammonium bromide and directly coated mesoporous shell, Powder Technology, 246520-529.
Maliyekkal S.M., Sreeprasad T.S., Krishnan D., Kouser S., Mishra A.K., Waghmare U.V., and Pradeep T., 2013, Graphene: A Reusable Substrate for Unprecedented Adsorption of Pesticides, Small, 9, 2, 273-283.
Maria Sarno C.C., Anna Garamella, Paolo Ciambelli., 2014, Synthesis and Characterization of Electrocatalyticgraphene/MoS2/Ni Nanocomposites, Chemical Engineering Transactions, 416, 169-175, DOI: 10.3303/CET1441037.
Myers J.P., Antoniou M.N., Blumberg B., Carroll L., Colborn T., Everett L.G., Hansen M., Landrigan P.J., Lanphear B.P., Mesnage R., Vandenberg L.N., vom Saal F.S., Welshons W.V., and Benbrook C.M., 2016, Concerns over use of glyphosate-based herbicides and risks associated with exposures: a consensus statement, Environmental Health, 15, 1, 1-13.
Rubí-Juárez H., Cotillas S., Sáez C., Cañizares P., Barrera-Díaz C., and Rodrigo M.A., 2016, Removal of herbicide glyphosate by conductive-diamond electrochemical oxidation, Applied Catalysis B: Environmental, 188305-312.
Xia S., Xu X., Xu C., Wang H., Zhang X., and Liu G., 2015, Preparation, characterization, and phosphate removal and recovery of magnetic MnFeO nano-particles as adsorbents, Environ Technology, 1-10.
Yamaguchi N.U., Bergamasco R., and Hamoudi S., 2016, Magnetic MnFe2O4–graphene hybrid composite for efficient removal of glyphosate from water, Chemical Engineering Journal, 295391-402.
Yao Y., Miao S., Liu S., Ma L.P., Sun H., and Wang S., 2012, Synthesis, characterization, and adsorption properties of magnetic Fe3O4@graphene nanocomposite, Chemical Engineering Journal, 184326-332.