Novel magnetic chitosan/graphene oxide/activated carbon composite beads for the removal of nonsteroidal anti-inflammatory pharmaceutical compound (Diclofenac) from aqueous solutions

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Introduction

Releasing of emerging pollutants into the environment without the proper treatment has received an increasing amount of attention in recent years, because of the detrimental effects they cause on aquatic assemblages and population health. Various methods, including physical and chemical treatments, have been used to remove pharmaceutical compounds from the wastewater. Adsorption is considered one of the most effective techniques. In the current work a novel composite material consisted of magnetic nanoparticles, chitosan, graphene oxide and activated carbon derived from pine cones (abbreviated hereafter as Mag Cs/GO/AC), was prepared in beads for the removal of a the pharmaceutical compound Diclofenac (Figure 1), under various experimental conditions. The effect of the adsorbent's dosage, pH value, contact time and initial concentration was examined with respect to Diclofenac removal in order to determine the efficiency of Mag Cs/GO/AC.

Results & Discussion

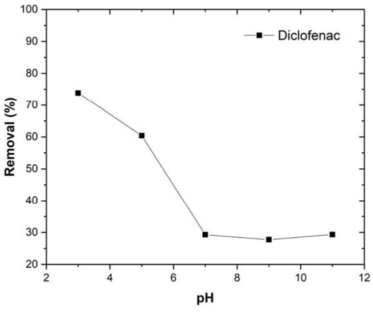

Figure 1: Effect of pH of Diclofenac adsorption on Mag Cs/GO/AC (C_0=50 mg/L, dose 1.0 g/L, T=30°C, contact time 24 h)

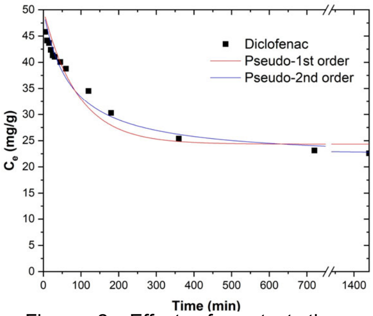

Figure 2: Effect of contact time of Diclofenac adsorption on Mag Cs/GO/AC (C_0=50 mg/L, dose 1.0 g/L , T=30°C, pH=5). Pseudo-1st and Pseudo-2nd order kinetic fitting.

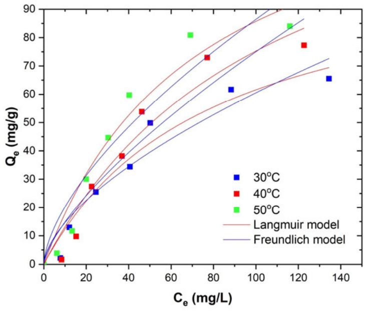

Figure 3: Isotherms (Dose 1.0 g/L, pH=5, t= 360 min)

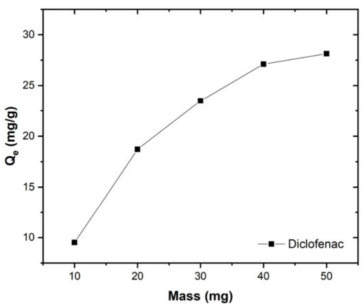

Figure 4: Efect of Mag Cs/GO/AC dosage (pH=5, t= 360 min , T=30°C)

Pseudo-2nd Order

K_2 (L/mg*min)	Q_e (mg/g)	R^2
0,0139	21,458	0,965

Langmuir isotherm model

T (°C)	Q_m (mg/g)	K_L (L/mg)	R^2
30°C	110,261	0,0126	0,968
40°C	157,772	0,0091	0,95
50°C	148,284	0,0137	0,955

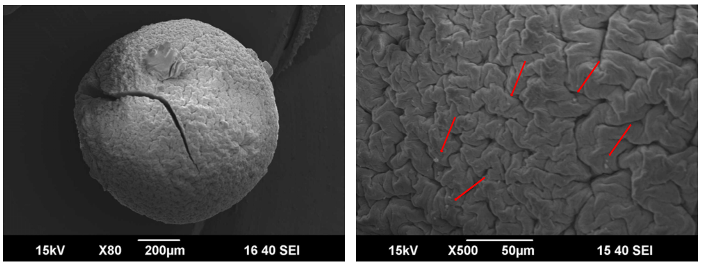

Figure 5: SEM Micrographs of Mag Cs/GO/AC

Batch experiments carried out to evaluate the ability of Mag Cs/GOAC to adsorb Diclofenac from aqueous solutions. Effect of pH revealed that the optimum removal took place at strongly acidic environments (Figure 1). As it can be observed from the kinetic experiments (Figure 2), equilibrium took place after 360 min of treatment. The experimental data presented a higher correlation coefficient with Pseudo-2nd order kinetic model, indicating the rate determining step of the overall process is chemisorption. Lastly, Langmuir model fit better with the data, indicating monolayer distribution of the adsorbate onto Mag Cs/GOAC surface (Figure 3).

The morphology of Mag Cs/GOAC identified with Scanning Electron Microscopy (Figure 5). The synthesis of this composite resulted in spherical beads of ~900 μm diameter. Sheet-like GO is partially embedded into the matrix of the bead, occasionally protruding to the external surface of the sphere. The texture of the bead results from Chitosan's rippling, while AC is observed as well distributed submicron particles on the surface (red arrows).

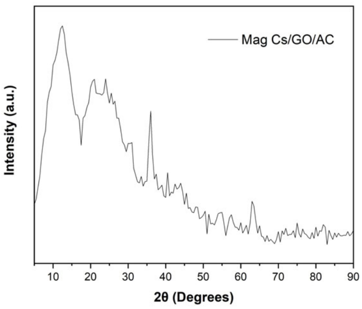

Figure 6: XRD of Mag Cs/GO/AC

The BET surface area (m²/g), average pore size (Å) and total pore volume (cm³/g) of Mag Cs/GOAC (Figure 7) were measured with N_2 porosimetry. As it can be observed, the composite material poses an extremely high surface area (1899 m²/g), which could be attributed to the presence of activated carbon. The XRD diffractogram confirmed the successful grafting of Mag Cs/GOAC .

SA (m²/g)	Avg Pore Size (Å)	Pore Volume (cm³/g)@STP
1899	24	231

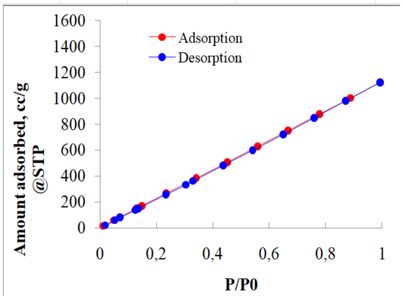

Figure 7: N_2 Porosimetry for Mag Cs/GO/AC

Conclusions

- Mag Cs/GO/AC beads were used for the removal of the pharmaceutical compound Diclofenac in batch experiments.
- It was found that at pH 5.0 ± 0.1, with the addition of 1.0 g/L the removal rate reached 62 %.
- The Langmuir isotherm model and the pseudo-second order kinetic model were found to better fit the adsorption (R^2= 0.968 and 0.965, respectively), concluding that the adsorption of Diclofenac on Mag Cs/GO/AC beads was monolayer and closer to chemisorption.
- The synthesis of Mag Cs/GO/AC led to a material with significantly high surface area.

Acknowledgment

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