Modified graphene oxide/chitosan composites for the adsorption of Methylene blue and Reactive black 5 from dyeing mixtures

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Introduction

Water pollution has been significantly increased the last decades, mainly because of the huge amount of insufficiently treated wastewater disposed in it. In terms of water pollutants, dyes are one of the main categories found in wastewaters. Their presence in aqueous media has been linked to serious adverse effects on aquatic fauna due to their recalcitrant nature, non-biodegradability and toxicity. Adsorption is one of the most effective techniques for the removal of dyes. In the current work a composite material consisted of chitosan and 0.5% graphene oxide (abbreviated hereafter as Cs/GO), was prepared for the removal of single component aqueous solutions and mixture of dyes (Methylene Blue and Reactive Black 5), under various experimental conditions. The effect of pH value, contact time and initial concentration was examined with respect to MB and RB5 removal in order to determine the efficiency of CS/GO composite.

Results & Discussion

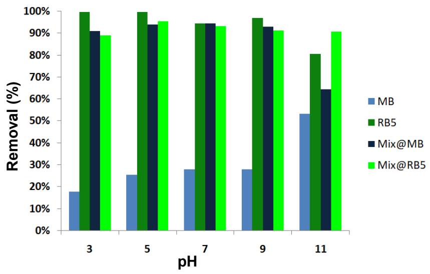


Figure 1: Effect of pH of MB & RB5 single component solution and mixture on Cs/GO (C_0=0.31 mmol/L, dose 1.0 g/L, T=30°C, contact time 24 h)

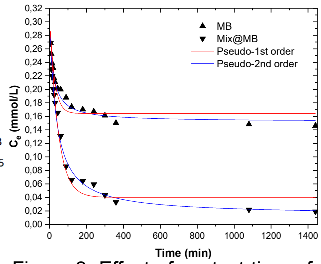


Figure 2: Effect of contact time of MB adsorption (single component & mixture) on Cs/GO (C_0=0.31 mmol/L, dose 1.0 g/L , T=30°C). Pseudo-1st and Pseudo-2nd order kinetic fitting.

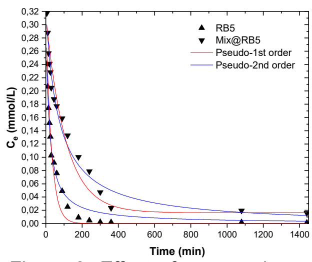


Figure 3: Effect of contact time of RB5 adsorption (single component & mixture) on Cs/GO (C_0=0.31 mmol/L, dose 1.0 g/L , T=30°C). Pseudo-1st and Pseudo-2nd order kinetic fitting.

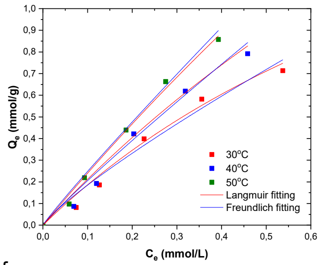


Figure 4: Isotherms for the removal of dyeing mixture from CS/GO (Dose 1.0 g/L, pH=5, t= 360 min). Langmuir and Freundlich fitting

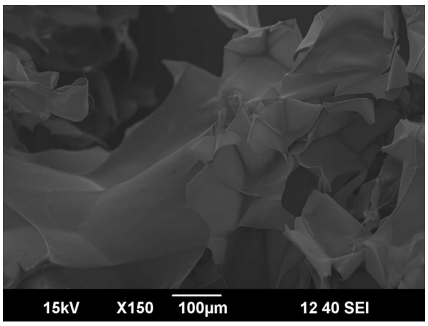


Figure 5: SEM micrograph of Cs/GO

Pseudo-2nd Order	K_2 (L/mmol*min)	Q_e (mmol/g)	R^2
MB	0,061	0,161	0,976
MIX@MB	0,031	0,299	0,988
RB5	0,066	0,313	0,985
MIX@RB5	0,012	0,311	0,981

Langmuir isotherm model

T (°C)	Q_m (mmol/g)	K_L (L/mg)	R^2
30°C	2,402	0,841	0,971
40°C	6,691	0,301	0,986
50°C	8,777	0,281	0,994

Batch experiments carried out to evaluate the ability of CS/GO to adsorb MB & RB5 from single component solutions and mixtures. Effect of pH revealed that the optimum removal took place at pH 5 for dye mixtures (Figure 1). As it can be observed from the kinetic experiments (Figures 3 & 4), the coexistence of the dyes in the solution alters the amount of adsorbed dyes, considerably increasing the removal of MB. 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 CS/GO surface.

The surface morphology of the material observed with Scanning Electron Microscopy (Figure 5). SEM micrographs revealed a sheet-like, smooth surface which is common for chitosan based materials. The incorporation of GO does not affect the smoothness of the surface probably due to the very small percentage of it (0.5%).

The BET surface area (m^2/g), average pore size (Å) and total pore volume (cm^3/g) of CS/GO (Figure 7) were measured with N_2 porosimetry. According to XRD pattern, the sample present two peaks at 2θ = 12.5° and 19° corresponding to graphene oxide and chitosan respectively.

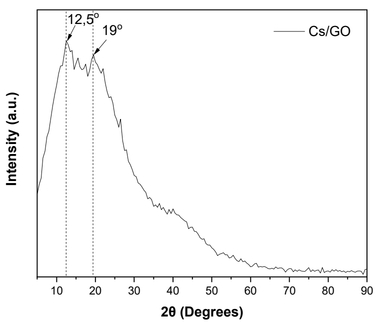
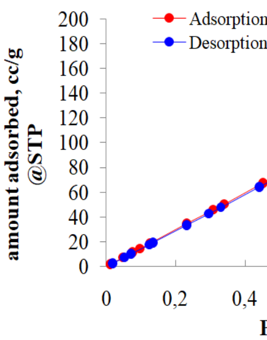


Figure 6: XRD of Cs/GO



SA (m^2/g)	Avg Pore Size (Å)	Pore Volume (cm^3/g)@STP
51.3	24	140

Figure 7: N_2 Porosimetry

Conclusions

- Cs/GO efficiently removed MB and RB5 from single component and mixture of the dyes solutions..
- It was found that at pH 5.0 ± 0.1, with the addition of 1.0 g/L the removal of MB and RB5 reached 95 %.
- Langmuir isotherm model and the pseudo-second order kinetic model were found to better fit the adsorption (R^2= 0.971, 0.988 (MIX@MB) and 0.981 (MIX@RB5), respectively), concluding that the adsorption of MB & RB5 on CS/GO was distributed as a monolayer and closer to chemical adsorption.

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Acknowledgment

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