Removal of reactive dye from wastewaters by adsorption onto aluminium modified activated carbon

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Introduction

Many industries, such as leather, textile, tanning, plastics, rubber, and cosmetics use huge amounts of synthetic dyes which may release into the wastewater in dyeing processes. Disposal of these wastewaters into the environment, without efficient treatment, causes serious damage to aquatic life. Furthermore, reactive dyes are recalcitrant, non-biodegradable, stable to oxidizing agents and toxic. Various methods, including physical and chemical treatments, have been used to remove these dyes from the wastewater. Adsorption on activated carbon has been found to be a very efficient technique. In the current work a novel composite material consisted of activated carbon and aluminum (abbreviated hereafter as AC-Al), was prepared for the removal of a commercial reactive dye (anionic and anthraquinonic) i.e. Reactive Black 5 (RB5) (Figure 1), under various experimental conditions. The effect of the adsorbent's dosage, pH value, contact time and initial RB5 concentration was examined with respect to RB5 removal in order to determine the feasibility of AC-Al.

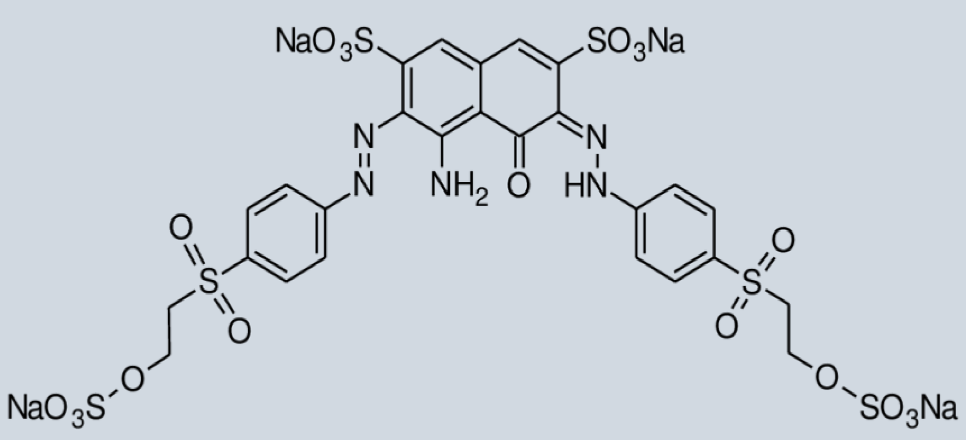


Figure 1: Structure formula of Reactive Black 5 (RB5) ($C_{26}H_{21}N_5Na_4O_{19}S_6$).

Results & Discussion

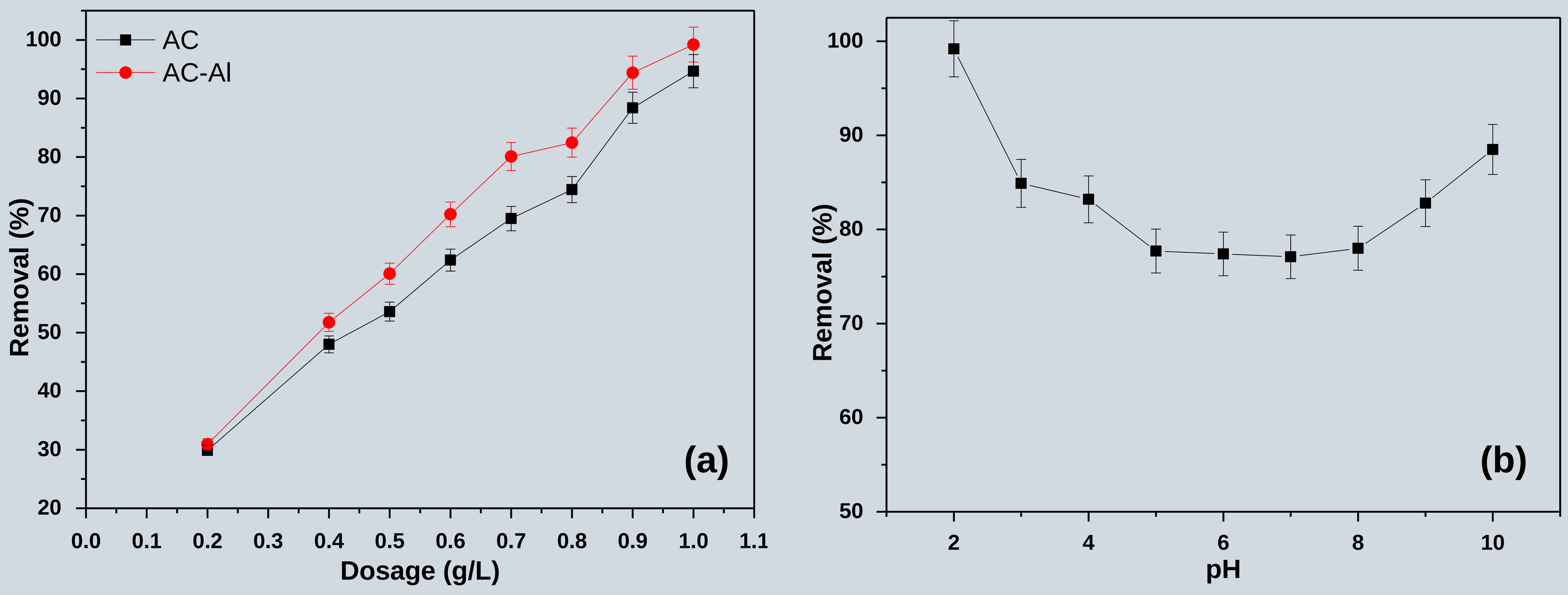


Figure 2: Effect of (a) AC-Al dose, in comparison with AC (pH 2); and (b) of initial solution pH on RB5 adsorption; initial RB5 concentration 100 mg/L, dose 1.0 g/L, T=298 K, contact time 24 h.

Activated carbon was synthesized from coconut shells (AC) and then modified with $AlCl_3$.
In batch experiments, the effect of the adsorbent's dosage and the initial solution pH were studied to determine the feasibility of AC-Al for RB5 removal. As illustrated in Figure 2, with the increase of the adsorbent's dosage, the percentage removal of RB5 increased from 30 % to 100 % at pH 2.0±0.1. The modification of the material showed advanced adsorption capacity, when comparing the results with those obtained by the use of the unmodified activated carbon (AC). The effect of pH was examined at pH range pH 2.0-10.0±0.1 with constant adsorbent's dose (1.0 g/L). As it can be noticed, the maximum dye removal was observed at pH 2.0±0.1.

In order to study the mechanism of adsorption and define the association between the concentration of RB5 and the adsorption capacity of the adsorbent, the adsorption isotherms models were conducted.
As shown in Figure 3a, the Freundlich isotherm model was found to better fit the adsorption, which describes the distribution of adsorption energy onto heterogeneous surfaces of the adsorbent. A relative high correlation coefficient (R^2 = 0.96), was found at pH 2.0±0.1. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models have been used for the kinetic study. The experimental data fitted better to the PSO kinetic model (Figure 3b), indicating that the adsorption of RB5 on AC-Al was closer to chemical adsorption.

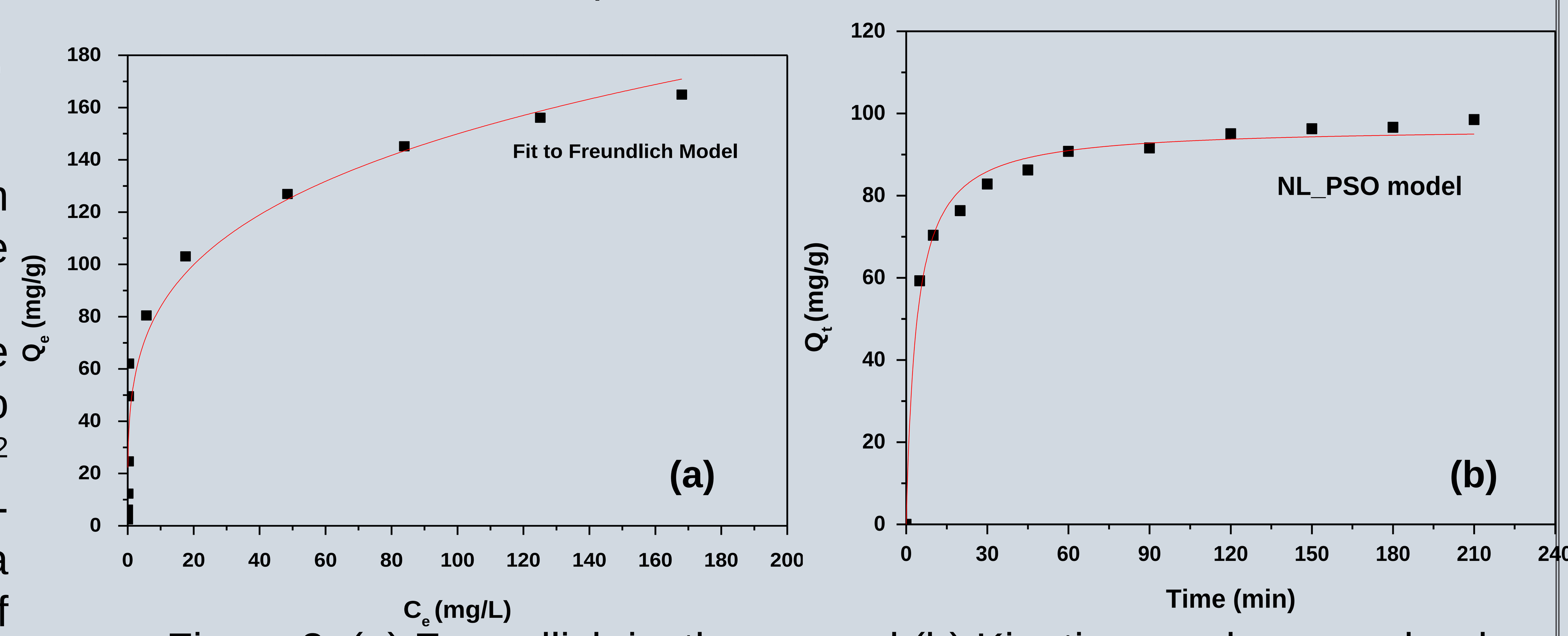
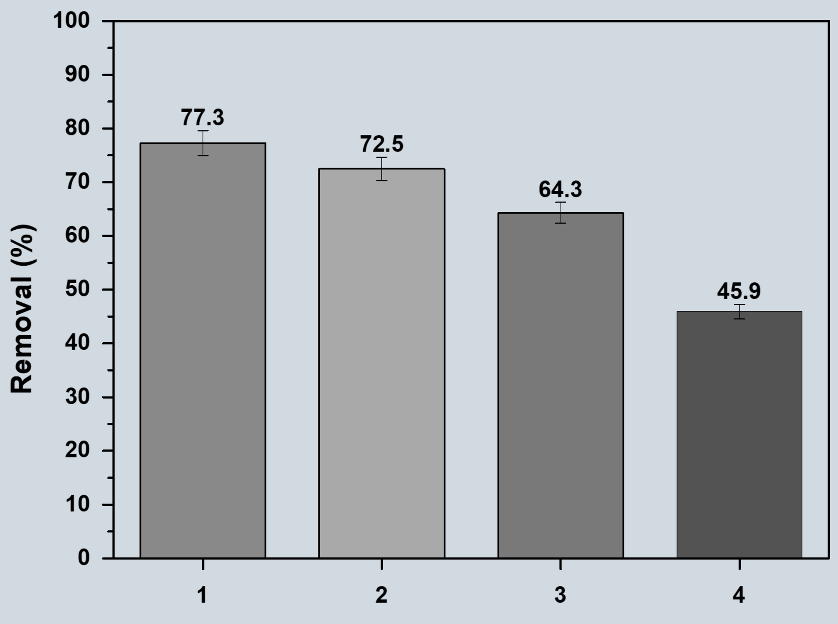


Figure 3: (a) Freundlich isotherms and (b) Kinetic pseudo-second order model for the adsorption of RB5 on AC-Al; dose 1.0 g/L, T=298 K.

Freundlich isotherm model			
1/n	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
0.25249	3.96058	46.869	0.96392

Pseudo-second order model (PSO)			
$Q_{e.exp}$ (mg/g)	K_2 (L/mg·min)	$Q_{e.cal}$ (mg/g)	R^2
103.069	0.0276	96.773	0.99087

The values of ΔH^0 and ΔS^0 were determined from the slop and intercept of the plot between ln(Kc) versus 1/T. A positive value of ΔH^0 suggests the endothermic nature of the process and ΔG^0 are negative recommending that the process is spontaneous. According to the positive value of ΔS^0, there is an increase in random interaction between solid/liquid interfaces, which is because the water molecules, which are displaced by the dye molecules, gain more entropy than is lost.



Regeneration experiments were applied to study the reusability of AC-Al for the removal of RB5 dye for four cycles, by using 1M NaOH treatment. According to Figure 4, there is a ~30 % reduction in its efficiency after 4 cycles.

Figure 4: Regeneration study; dose 0.8 g/L, pH 2.0±0.1, contact time 3 h

Thermodynamic parameters for the adsorption of RB5 onto AC-Al; initial RB5 concentration 100 mg/L, dose 0.8 g/L, pH 2.0±0.1, contact time 1.5 h

T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol·K)	R^2
298	-2.474			
308	-2.767	62.621	0.0293	0.9970
318	-3.060			

Conclusions

- Activated carbon from coconut shells was used after modification with aluminum salts, for the removal of a commercial reactive dye, Reactive Black 5 (RB5).
- It was found that at pH 2.0 ± 0.1, with the addition of 1.0 g/L the removal rate reached 100 %.
- The Freundlich isotherm model and the pseudo-second order kinetic model were found to better fit the adsorption (R^2= 0.96 and 0.99, respectively), concluding that the adsorption of RB5 on AC-Al was multilayer and closer to chemisorption.
- According to thermodynamics, there is a positive value of ΔH^0 (62.621 kJ/mol) that suggests the endothermic nature of the process.
- Finally, a reuse of AC-Al adsorbent for four cycles after successfully regenerated, was achieved.

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