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Adsorption modeling and optimization of crystal violet a cationic dye in batch reactor

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ABSTRACT: Graphene oxide nano-sheets were synthesized using modified Hummer's method and characterized using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and Fourier Transform Infra-Red (FTIR) analyses. Response surface methodology (RSM) was used to optimize the effects of the effective factors including pH (4-9), adsorbent dosage (0.05-0.4 g/L), initial dye concentration (50-400 mg/L), and temperature (10-40 C°) in batch adsorption reactor. The adsorption capacity of graphene oxide and removal percentage of crystal violet in the optimum condition (pH of 7.4, the adsorbent dosage of 0.19 g/L, the initial concentration of 100 mg/L, and temperature of 30.4 C°) were predicted by the polynomial regression model to be 474 mg/g and 90%, respectively. Dye initial concentration and the adsorbent dosage with 51.6 and 41.7% respectively, showed the most percentage of contribution among the effective factors. Adsorption kinetic was investigated using pseudo-first order, pseudo-second order, and intraparticle diffusion kinetic models. Adsorption isotherm also was studied using Freundlich and Langmuir isotherm models. Results demonstrated the high correlation of adsorption kinetic and isotherm with pseudo-second order and Langmuir models respectively. In addition, the thermodynamic study indicated the endothermic and spontaneous nature of adsorption.

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1-Introduction

The control of water pollution has become one of the most significant environmental problems in recent years. Nowadays, synthetic dyes are considered as highly toxic environmental pollutants because of their toxicity and high stability to the biodegradation. Crystal violet as ac cationic basic dye is widely used for many purposes such as textile, medical. pH indicator etc. [1]. Most of the organic dyes have aromatic rings in their structure that, make them very toxic and non-biodegradable [2]. So removal of this dyes from industrial effluents before discharging in natural waters is very important.

Herein, Graphene oxide (GO) was synthesized by using modified Hummer's method, containing oxidation of graphite in the presence of strong oxidants at different temperatures. The synthesized GO was then characterized and used for batch adsorption of Crystal violet (CV) from synthetic and real wastewater.

2. Methodology

GO nano-sheets were synthesized by using modified Hummer's method and then characterized by using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR).

Response Surface Methodology (RSM) was used to design adsorption runs and optimize the effects of the adsorption parameters including pH (4-9), adsorbent dosage (0.05-0.4 g/L), initial dye concentration (50-400 mg/L), and adsorption temperature (10-40 °C) in the batch adsorption reactor. Analysis of variance (ANOVA) was employed to investigation adequacy and significance of the model, percentage of contribution, and interactions between the independent variables.

Adsorption kinetic was investigated by using three common kinetic models including pseudo-first order, pseudo-second order, and intraparticle diffusion. Adsorption isotherm was modeled using Freundlich and Langmuir isotherm models. In addition, thermodynamic parameters including enthalpy, entropy, and Gibbs free energy were calculated.

Real wastewater experiment was performed in optimum condition in order to investigate performance of GO for removal of cationic dyes in presence of other ions.

3. Results and Discussion

The morphology, bonds and structure of synthesized GO have been presented in Figure 1. This figure shows sheet-like structure and presence of the oxygen containing groups in the surface of adsorbent. It also proves effective oxidation of the GO in contact with strong oxidants. In addition, Figure 1d confirms adsorption of CV on the surface of GO [3-5].

The Adsorption capacity of GO and removal percentage of CV in the optimum condition (pH of 7.4, the adsorbent dosage of 0.19 g/L, the initial concentration of 100 mg/L, and temperature of 30.4 C°) were predicted by the polynomial regression model to be 474 mg/g and 90%, respectively. According to the ANOVA results, the value of Fcal (68.1) was much more than Ftab (2.46) and also p-value (0.0001) was lower than 0.05 and it suggested significance and suitability

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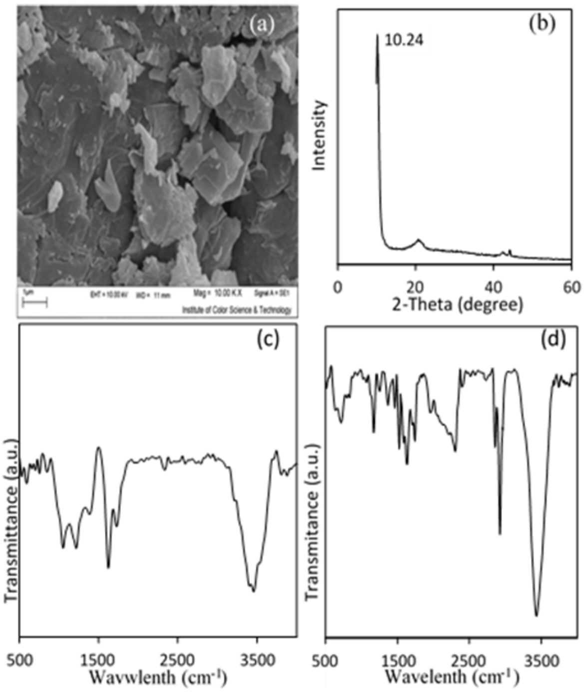

Figure 1. Scanning electron micrographs (a), X-ray diffraction patterns (b), and FTIR spectra of the synthesized GO before (c) and after (d) CV adsorption.

of the quadratic model [6, 7]. Dye initial concentration and the adsorbent dosage showed the most percentage of contribution among the effective factors with 51.6 and 41.7% respectively (Figure 2).

Adsorption kinetic showed a significant correlation to the pseudo-second order model (R2=1), with an excellent prediction of adsorption capacity [8]. Adsorption isotherm modeling showed a high correlation to Langmuir isotherm model (R2=0.998). This model also predicted maximum adsorption capacity of GO very well [9]. In addition, the thermodynamic study indicated the endothermic and spontaneous nature of adsorption [3]. Finally, the real wastewater experiment at the optimum condition showed high performance of adsorbent in presence of other ions (R=88%).

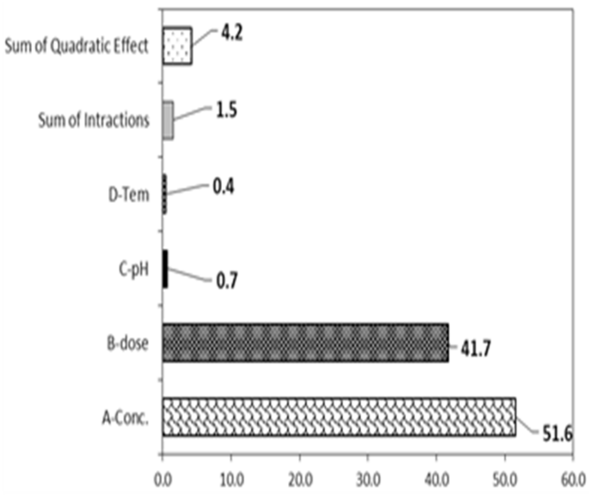

Figure 2. Percentage of contribution (PC%) values for the effective parameters of adsorption

4. Conclusions

Results of the present research confirmed GO as a highly effective adsorbent for removal of cationic dyes from aquatic media. Adsorption capacity and removal percentage in the optimum condition were predicted to be 474 mg/L and 90% respectively. Adsorption kinetic and isotherm data were fitted to pseudo-second order kinetic model and Langmuir isotherm model respectively. Endothermic and spontaneous nature of the adsorption process also were indicated study of the thermodynamic parameters. In addition, performance of the adsorbent for removal of CV from real wastewater and in presence of other ions was proved by real wastewater adsorption experiment in the optimum condition.

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