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Research Paper

Fabrication of dolomite adsorbent processed with chitosan and graphene oxide for methylene blue removal from water

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1. ABSTRACT
In this study, a new composite adsorbent based on dolomite mineral, coated with chitosan and graphene oxide was fabricated and used for removal of methylene blue (MB) from water. The effects of time, initial MB concentration, pH and temperature on the adsorption capacity of the fabricated composite adsorbent in the removal of MB as a cationic dye were investigated. The obtained results were analyzed by Freundlich and Langmuir isotherm models as well as pseudo first and second order kinetic models. The results of adsorption experiments showed that the fabricated composite adsorbent for removing MB follows the Langmuir adsorption isotherm model and the pseudo second order kinetic model. According to the Langmuir isotherm, the maximum monolayer adsorption capacity of MB on the surface of the composite adsorbent is equal to 3.746 mg/g. This adsorbent has a higher adsorption capacity at high temperatures and alkaline pHs.

Keywords: Adsorption, Dolomite, Water treatment, Methylene Blue, Chitosan, Graphene oxide.

2. INTRODUCTION
Clean water is a vital element for the survival of living organisms. The presence of various pollutants such as dyes, heavy metal ions, organic substances and bacteria in water is considered a serious threat to human health. Dyes are the most important sources of water pollution. Excessive exposure to dyes causes skin diseases and respiratory problems, and in some cases increases the risk of cancer in humans [1]. Therefore, providing clean water through wastewater treatment using various separation processes is very important. Adsorption process is a very popular method for colored wastewater treatment due to its high efficiency and simplicity. Nowadays, development of new adsorbents with high adsorption capacity from minerals has attracted the attention of many researchers [2]. Dolomite with chemical formula of $CaMg(CO_3)_2$ is one of the carbonate minerals that can be effectively used as an adsorbent [3]. Chitosan with high hydrophilicity, favorable chemical resistance, availability and biocompatibility can also be effectively used as an adsorbent to treat all types of colored wastewater [4]. Graphene oxide (GO) with high absorption capacity, high surface active sites, high surface area and large amounts of hydrophilic functional groups such as hydroxyl, carboxyl, epoxy, etc can also be effectively used as an adsorbent [5].

In the present study, dolomite ore was calcined at temperature of 900°C. The calcined dolomite was processed by chitosan and GO solution and the obtained composite adsorbent was used to remove methylene blue (cationic dye) from water. The effect of time, initial dye concentration, pH and temperature on the adsorption capacity of the composite adsorbent was investigated. The obtained results were analyzed by Freundlich and Langmuir isotherms as well as pseudo first and second order kinetic models.

3. MATERIALS AND METHODS
After crushing, sieving, washing and drying of dolomite, 50 gr of the obtained dolomite was calcined at 900°C. Then, 0.1 gr of GO was dispersed in 100 ml acetic acid solution with 1 v.% concentration for 15 min using an ultrasonic probe. Then, 1 wt.% chitosan was added to the mixture and stirred at 400 rpm for 24 h until chitosan was completely dissolved. Then, the calcined dolomite was immersed in the resulting solution for 1 h and then the dolomite particles were separated from the solution and dried at room temperature for 24 h. Finally, the prepared composite adsorbent was annealed at 90

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°C for 1 h. Three samples of raw, calcined and composite dolomite were characterized by FESEM, FTIR and BET analyzes.
Adsorption experiments were performed to investigate the effects of time, initial methylene blue (MB) concentration, temperature and pH. 0.5 gr of the adsorbents were added to 100 mL MB solution with a certain concentration and pH and placed on a shaker at 100 rpm for 3 h at a certain temperature. The MB concentration of the samples was measured using a UV spectrophotometer (Metertech: SP8001) at a wavelength of 665 nm.

4. RESULTS AND DISCUSSION

FTIR spectra of the raw, calcined and composite dolomite samples are shown in Figure 1. FTIR spectra of the raw dolomite samples, the peaks at 1412 and 872 cm^{-1}, which can be seen in all natural samples of dolomite, belong to the carbonate groups. Peaks at 740 and 350 cm^{-1} belong to the sulfate groups. As can be seen in Figure 1 (b), the calcined dolomite spectrum does not show any peaks in the wave number of 400 to 4000 cm^{-1}. This shows that the calcination process of dolomite is well done. As can be seen in Figure 1 (c), the peak at 3650 cm^{-1} in the composite dolomite spectrum is related to the hydroxyl (OH) and amine (NH_3) groups. The presence of these functional groups shows that dolomite is well functionalized and can be used as an absorbent of MB as cationic dyes.

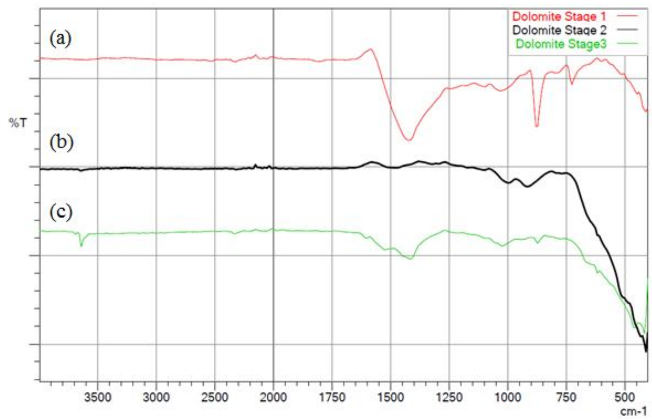

Figure 1. FTIR spectra of the (a) raw, (b) calcined and (c) composite dolomite samples

FESEM images of the raw, calcined and composite dolomite samples are shown in Figure 2. As can be seen, after calcination, the porosity of the dolomite structure has increased due to carbon dioxide gas release from the dolomite structure. The composite dolomite has a heterogeneous structure and chitosan particles and GO sheets can be seen on the dolomite surface, which is shown by the arrow in Figure 2 (d).

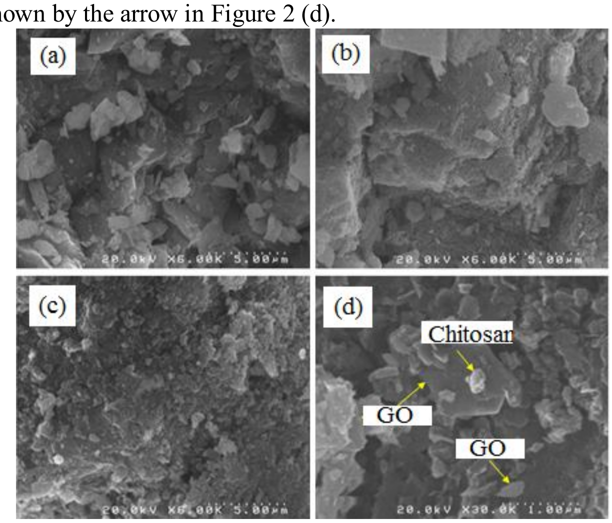

Figure 2. FESEM images of the (a) raw, (b) calcined and (c) composite dolomite samples

BET analysis of the raw, calcined and composite dolomite samples are presented in Table 1. As can be seen, compared to the raw dolomite, the specific surface area, the pore volume (porosity) and the average pore diameter of the calcined and composite dolomite samples have increased, significantly.

Table 1. BET results of the dolomite samples

Samples	Pore valume (cm^3/g)	Specific surface area (m^2/g)	Average pore diameter (nm)
Raw dolomite	0.008	0.61	50.43
Calcined dolomite	0.061	12.78	170.12
Composite dolomite	0.047	11.65	112.34

Effects of time, initial MB concentration, pH and temperature on the adsorption capacity of the composite adsorbent are shown in Figure 3. As can be observed, the composite adsorbent has higher adsorption capacity at high initial MB concentration, pH and temperature.

The obtained adsorption results were analyzed by Freundlich and Langmuir isotherm models as well as pseudo first and second order kinetic models. It was found that the fabricated composite adsorbent for removing MB follows the Langmuir adsorption isotherm model and the pseudo second order kinetic model. According to the Langmuir isotherm, the maximum monolayer adsorption capacity of MB on the surface of the composite adsorbent is equal to 3.746 mg/g.

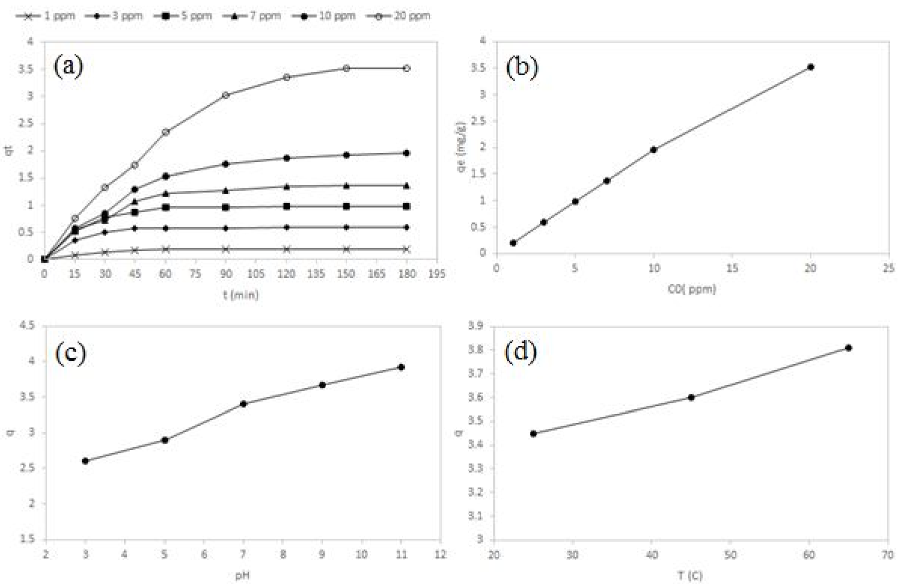

Figure 3. Effects of (a) time, (b) initial MB concentration, (c) pH and (d) temperature on the adsorption capacity of the composite adsorbent

5. CONCLUSION

In this research, a new composite adsorbent based on dolomite mineral, coated with chitosan and GO was made and the performance of this adsorbent in removing MB from water was investigated. The effects of the time, initial MB concentration, pH and temperature on the adsorption capacity of the composite adsorbent in the removal of the MB were investigated. The results of adsorption experiments showed that the fabricated composite adsorbent for removing MB follows the Langmuir adsorption isotherm model and the pseudo second order kinetic model. According to the Langmuir isotherm, the maximum monolayer adsorption capacity of MB on the surface of the composite adsorbent is equal to 3.746 mg/g.

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