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ORIGINAL ARTICLE

A promising strategy for the utilization of waste nitrile gloves: cost-effective adsorbent synthesis

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Abstract

Acrylonitrile butadiene rubber (NBR) glove wastes were converted into a cost-effective adsorbent through a facile carboxylation reaction and used for the removal of cationic methylene blue (MB) dye from aqueous solutions frequently encountered in the polluted waters. Characterization of the adsorbent was realized by Fourier transform infrared (FTIR) spectroscopy and thermogravimetry (TGA) to identify the functional groups and the thermal stability. Kinetic and thermodynamics studies were carried out for the evaluation of important adsorption parameters. The effect of solution pH, concentration and temperature were also investigated for determining the optimum adsorption conditions. The kinetic model was found to be in harmony with the first order kinetic model and adsorption model was well fitted with Freundlich isotherm. Maximum adsorption capacity was reached to 60 mg/g in 24 h at 318 K for 1.10^{-3} molar MB with pH 9. Thermodynamic parameters revealed that adsorption is in chemisorption range, spontaneous and exothermic in nature. The study showed that waste nitrile gloves could be successfully benefited as an efficient and low cost polymeric material for the adsorption of organic dyes from industrial discharged polluted waters.

Keywords Methylene blue · NBR gloves · Freundlich isotherm · Adsorption · First-order kinetic model

Introduction

NBR gloves are made of synthetic rubber (acrylonitrile butadiene copolymer). They contain no natural proteins and offer excellent resistance to many types of corrosive chemicals [1]. These gloves are heavily used in daily life from laboratory to home use and its waste is non degradable and a growing problem for environment and economy [2]. To overcome the accumulation of this type pollution, recycling is the generally preferred method in which waste NBR gloves are mixed with virgin acrylonitrile butadiene rubber in a fixed ratio to produce value-added materials but the resulting properties of final product are inferior when compared to the virgin rubber [1, 3]. Diversifying of efficient and more useful benefiting method from NBR wastes is an important matter for researches. In this respect, utilizing the NBR wastes as an economical adsorbent material could be a promising method for the removal of contaminants from industrial waste effluents. The most common of these contaminants are the toxic dye molecules discharged from factories such as textile, leather, plastic, food, paper, pigments. Methylene blue (MB) as a good representative of cationic dyes is a frequently used coloring agent for several applications with some negative impacts on human, animal and aquatic life such as irritation of mouth, throat, oesophagus and stomach with symptoms of nausea, vomiting and diarrhea [4]. Therefore, removal of MB from wastewater by cost-effective adsorbents is an important concern from environmental point of view. Agricultural biosorbents such as pine cone [5], weeping willow [6], Limonia acidissima [7] and mango leaf powder [8] and industrial wastes such as red mud [9] and fly ash [10, 11] are recently proposed cost-effective and non-conventional adsorbents.

In this study, wastes of heavily used NBR gloves have been converted to a polymeric adsorbent material for the first time and proved as an economical alternative to existing materials for treatment of dye contaminated industrially discharged waters. By a very facile reaction of concentrated sulfuric acid and NBR gloves, an efficient material

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has been created for removal of dye contaminants. Through the evaluation of kinetics, thermodynamic parameters and maximum capacity of the adsorption the material have been characterized.

Materials and methods

Chemicals

Sulfuric acid and sodium hydroxide were purchased from Fluka and Merck for carboxylation reaction of nitrile groups. Methylene blue dye (Fig. 1) was taken from Merck. All reagents were of analytical reagent grade and used without any further purification.

Adsorbent preparation

Before carboxylation, NBR gloves thickness of which is 0.12 mm were throughly washed with deionized water, treated with isopropyl alcohol for removal of organic contamination on the surface and were immersed in 95% sulfuric acid for 15 min. At the end of the reaction carboxylated NBR gloves (R-NBR) were filtered, washed with excess water, neutralized with concentrated sodium hydroxide (10 M) and again washed with deionized water for several times and dried at 90 °C for 1 day. The reaction pathway and creation of carboxylic acid groups were illustrated in Fig. 2.

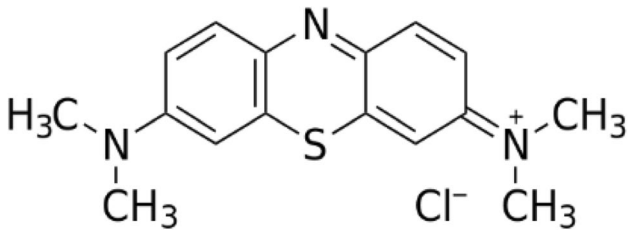

Fig. 1 Molecular structure of methylene blue

Adsorption studies

Kinetic studies

Kinetic studies of the adsorption process were carried out at 318 K and 1.10^{-3} mol/L methylene blue concentration at pH 9. A predetermined amount of adsorbent (0.05 g) was used in the batch experiments. At suitable intervals, absorbance of the supernatants was followed by UV–Vis spectrometer at 664 nm. The adsorption data were tested according to the pseudo-first-order (Eq. 1) and pseudo-second-order (Eq. 2) kinetic models [5, 12]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

$$\frac{1}{q_t} - \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t, \tag{2}$$

where q_t and q_e represent the amount of dye adsorbed (mg/g) at any time t and at equilibrium time, respectively, k_1 and k_2 represent the adsorption first-order and second-order rate constants (1/min and g/mg min) and t is the contact time (min). The adsorption rate constants k_1 and k_2 were calculated from the plot of t against log $(q_e - q_t)$ and $1/q_t$, respectively.

The amount of the dye adsorbed at time t and at equilibrium time, q_t (mg/g) and q_e (mg/g) were calculated by the following equation [12]:

$$q_{tore} = \frac{(C_0 - C_{tore})V}{m}, \tag{3}$$

where C_o is the initial dye concentration (mg/L), C_t is the concentration of the dye at time t. V is the volume of the solution (L) and m is the mass of the adsorbent (g).

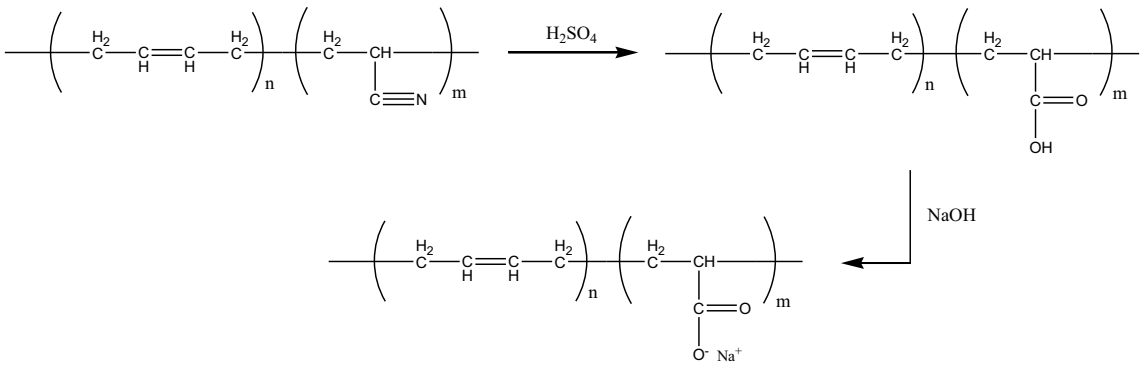

Fig. 2 Conversion of nitrile groups into carboxylate groups

Adsorption isotherm

Adsorption characteristics were identified by fitting with Freundlich and Langmuir isotherm models using three different dye concentrations 1.10^{-3}, 2.10^{-3} and 4.10^{-3} mol/L at pH 9 and 318 K. Freundlich isotherm model can be expressed in its linear form by the following equation [12]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \tag{4}$$

A plot of ln C_e against ln q_e gives a linear plot where q_e is the amount of dye adsorbed per unit of adsorbent at equilibrium time (mg/g) and C_e is equilibrium concentration of dye in solution (mg/L). K_f and n are the isotherm constants which indicate the capacity and the intensity of the adsorption, respectively [12].

Langmuir isotherm model in its linear form can be given by the following equation [5]:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_a q_m}\right) + \frac{C_e}{q_m}, \tag{5}$$

where q_m is the maximum adsorption capacity (mg/g) and K_a is the value for Langmuir constant related to the energy of adsorption (L/mg) is predicted from the intercept of the linear plot between C_e/q_e versus C_e.

Thermodynamic parameters

From the point of physical chemistry, adsorption process is best defined with Gibb's free energy (ΔG^o), enthalpy of adsorption (ΔH^o) and the entropy (ΔS^o) change where ΔG^o explains spontaneity of the process, ΔH^o is an indication of physical or chemical adsorption process, and ΔS^o is the randomness of the process. The mentioned thermodynamic parameters are calculated by the following equations [12]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \tag{6}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}, \tag{7}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration (mg/L), T is the temperature in K and R is the gas constant (8.314 J/mol K).

Results and discussion

Adsorbent characterization

FTIR analysis was performed with Perkin-Elmer BX-II model spectrometer. Absorbance spectra were collected between 4000 – 400/cm with 50 scans and are given in Fig. 3a, b. In the spectrum of NBR (Fig. 3a), characteristic bands of nitrile group were observed at 2236/cm. The band at around 3414/cm shows OH bond vibrations. The absorptions at 2848, 2922, 1438 1357 and 969/cm represent the symmetric, asymmetric and deformation vibrations of the C–H bonds. The band at 1606/cm corresponds to C=C in butadiene groups in the polymeric chain [13–17].

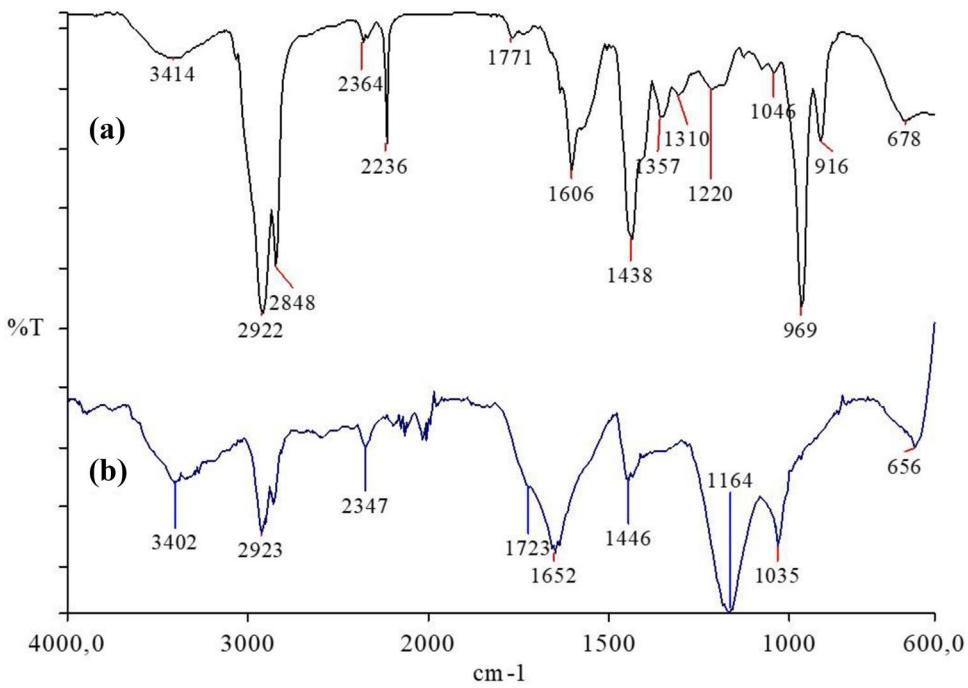

Fig. 3 FTIR spectrum of NBR (**a**) and R-NBR (**b**)

As in Fig. 3b, the main important changes were observed at the bands 2347, 1723, 1652 and 1164/cm. The increasing intensity of the band at 1652/cm and the appearance of new bands at 1723 and 1164/cm (characteristic –COOH groups) together with the decreasing intensity of the band at 2347/cm (nitrile group) clearly shows the success in the conversion of nitrile groups to carboxylate groups [18, 19].

The thermal stability of the waste NBR glove and R-NBR was determined using Perkin-Elmer Diamond TG/DTA analyzer in aluminum pans under nitrogen atmosphere between 40 and 600 °C at a heating rate of 10 °C/min. As can be seen from Fig. 4, one step decomposition of the both rubbers take place nearly at the same temperature (~450 °C).

The mass loss at about 100 °C in the thermogram of R-NBR indicated that the structure adsorbed below %1 water. It can be claimed that there is no negative effect of functionalization on thermal stability of the waste rubber and therefore can be used at adsorption processes which are carried out at much higher temperatures.

Physical chemistry of adsorption

Adsorption process on 0.05 g samples was tested for three different temperatures and MB concentrations (275, 298, 318 K and 1.10^{-3}, 2.10^{-3}, 4.10^{-3} mol/L) at pH values of 3, 7 and 9. With respect to the meaningful adsorption kinetics and modeling higher MB concentrations were eliminated due to low adsorption values and the measurement difficulty in UV spectrophotometer (Fig. 5). Hence, adsorption parameters were followed with 1.10^{-3} mol/L. Optimum conditions were determined according to the changing adsorption percentages for 24 h (equilibrium time). As seen from Fig. 6, increasing pH and temperature have positive effect on adsorption process and ideal conditions were chosen as pH 9 and 318 K.

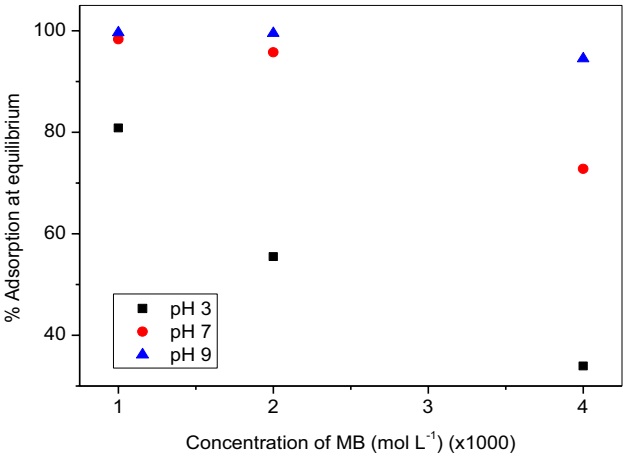

Fig. 5 Effect of MB concentration on adsorption

To evaluate the adsorption and kinetic models, batch adsorption experiments were carried out at different time intervals. Data produced in this way were applied to the linear forms of Freundlich and Langmuir isotherm equations. The corresponding r^2 values of the linear plots have supported Freundlich isotherm (Fig. 7, $r^2=0.96$) which is higher than that of Langmuir isotherm (Fig. 8, $r^2=0.21$).

Maximum adsorption capacity (K_f) and intensity of adsorption (1/n) were determined as 60 mg/g and 0.94, respectively. 1/n value shows that when the concentration of MB increases, the relative adsorption decreases as a sign of saturation of adsorption sites available to MB. 1/n value is an indication of surface heterogeneity and a measure of adsorption intensity which changes between 0 and 1. If it is near one, it is a sign of homogeneous surface and surface heterogeneity increases if it goes to zero. As the value of 0.94 is near one, it means that MB molecules are adsorbed

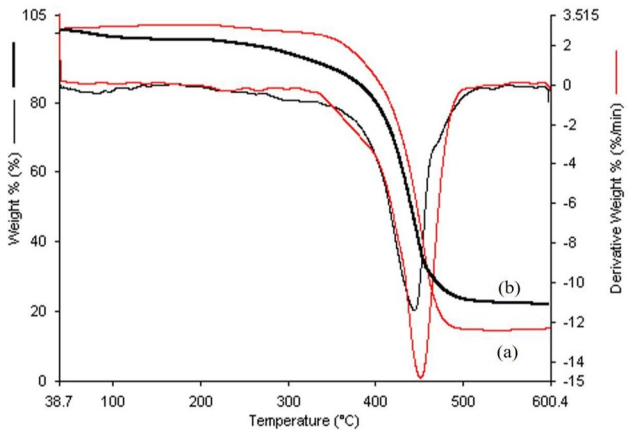

Fig. 4 TG/DTG curves of NBR (**a**) and R-NBR (**b**)

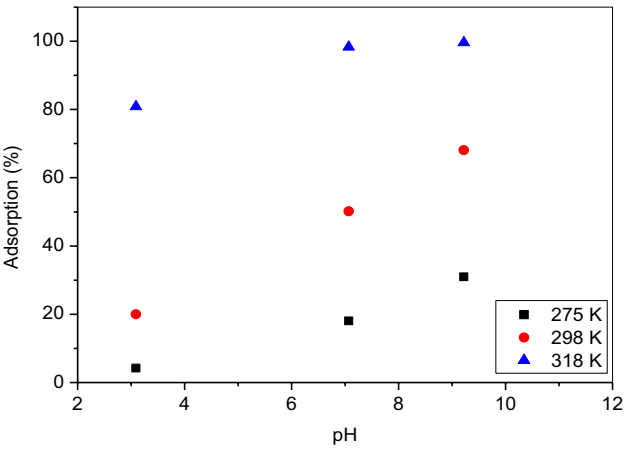

Fig. 6 Adsorption percentages at three different temperatures

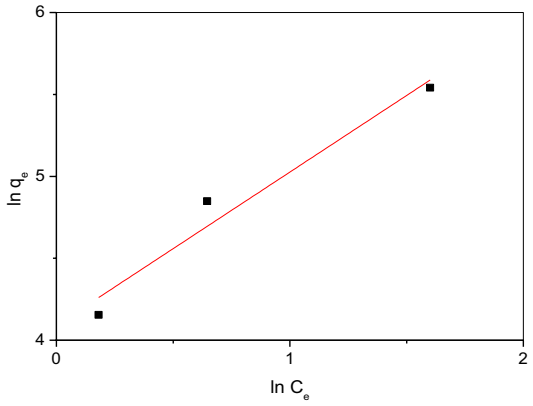

Fig. 7 Linear fit of adsorption data to the Freundlich isotherm

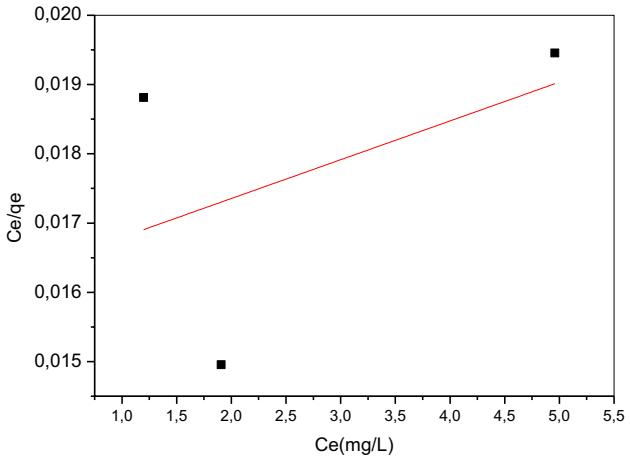

Fig. 8 Linear fit of adsorption data to the Langmuir isotherm

Table 1 Adsorption capacities of some low cost adsorbents

Adsorbent	Adsorbent capacity(mg/g)	References
Redmud	274	[9]
Mango leaf powder	156	[8]
Limonia acidissima	81	[7]
Weeping willow	61	[6]
Acid-treated pinecone	40	[5]
Flyash	8	[10]
R-NBR	60	(Present study)

at nearly smooth surface which all of them are at the same adsorption energy.

Adsorption capacity of the R-NBR was shown to be relatively higher than many other low-cost adsorbent materials (Table 1).

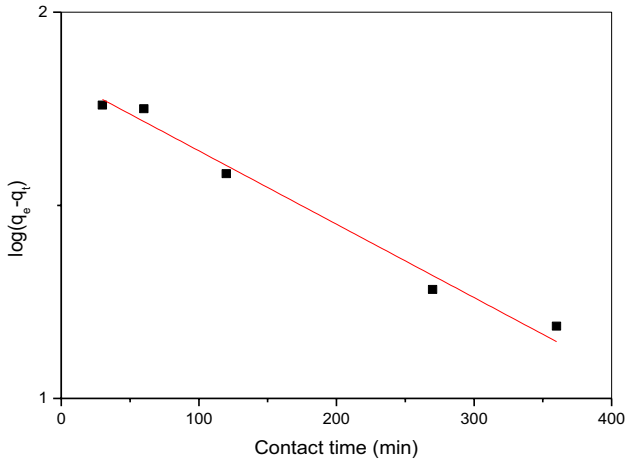

Fig. 9 Pseudo-first-order kinetic linear fit ($r^2 = 0.98$)

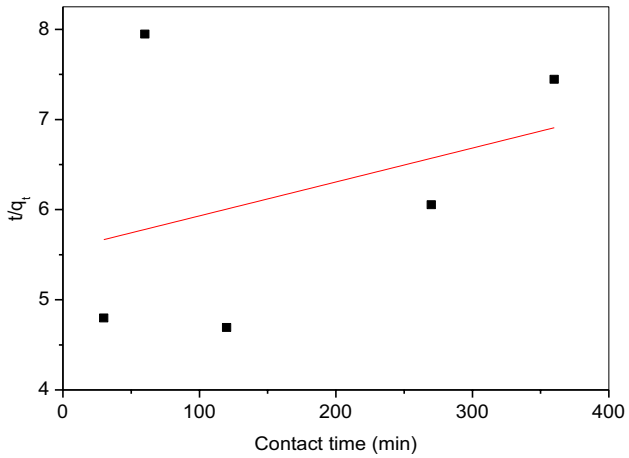

Fig. 10 Pseudo-second-order kinetic linear fit ($r^2 = 0.13$)

As seen from Figs. 9 and 10, r^2 values for the linear plot of pseudo-first-order kinetic are higher than the pseudo-second-order model. The rate constant of the adsorption was found as 0.0044/min which is roughly at the same level with the most cost-effective adsorbent systems such as pith, orange peel, leaf powder [20]. Therefore, kinetic model of the adsorption process corresponds to pseudo-first-order kinetics which indicates that the mechanisms of adsorption are in harmony with physisorption that is the interaction of positively charged methylene blue molecules and negatively charged carboxylate groups on the polymer backbone created by sulfuric acid treatment of the –CN groups. In the pseudo-first-order kinetics, the pseudo word is used because there are two molecules in the adsorption process one is water molecule and other is the methylene blue molecule. Normally the reaction kinetics have to follow second-order kinetics, but we use water as solvent, the amount of which is much higher than the MB molecules, therefore the order

Table 2 Thermodynamic parameters of the adsorption

Temperature (K)	ΔH^{o} (kJ/mol)	ΔG^{o} (kJ/mol)	ΔS^{o} (J/molK)
318	− 26,230	− 10.51	294
298	− 24,581	− 6.19	
275	− 22,685	2.26	

of adsorption kinetics is reduced to first order named as pseudo-first-order kinetics. Due to the strong interaction of positive charges of MB molecules and negative charges of carboxylated groups of the polymer backbone, MB molecules are readily adsorbed on the available sites around the carboxylated groups, and hence fast changes occur in the concentration of the MB molecules in harmony with the first order.

Thermodynamic parameters of the adsorption were collected in Table 2. The Gibbs free energy of the adsorption turns to negative values above 275 K and the adsorption process becomes spontaneous due to the increasing polymer chain mobility with temperature. From the negative values of enthalpy, it can be claimed that adsorption process is exothermic in nature. The positive value of entropy demonstrated that adsorption is a random process at the solid-adsorbent/liquid-solvent interface. Since increasing temperature makes the adsorption process more exothermic and spontaneous, the favorable temperature among the others has been determined as 318 K for the adsorption of the MB on R-NBR. By taking account of all adsorption data, strong ionic attraction process (inferred from relatively high ΔH values) is the main reason for sorption that occurs between negatively charged side groups on the polymer backbone and cationic dye molecules.

Conclusion

This study proved that functionalization of waste NBR glove to be used as adsorbent material is a good strategy for a new type of waste management method and resulted in a promising cheap adsorbent for the removal of cationic MB dye from aqueous solutions with a comparatively high adsorption capacity (60 mg/g).

Thermodynamic parameters of the adsorption showed that adsorption process turns to be spontaneous above 275 K due to the decreasing number of hindered side groups by increasing temperature which then will be an attraction center for positively charged MB molecules. Highly negative values of adsorption enthalpy reveal that the process is exothermic with a positive entropy value indicating that adsorption occurs in a random way to an extent. The best adsorption conditions for this material were determined as 318 K, pH 9 and 1.10^{-3} mol/L MB concentration at 24 h. The Freundlich isotherm is the best fitting model for the adsorption and kinetics of the process is well fitted with pseudo-first-order kinetic model which will also supports that the process is carried out on a strong physical interaction.

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