JAEHR Journal of Advances in Environmental Health Research

The study of azo dye removal from liquid medium by modified clay

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Original Article

Abstract

In this batch study, montmorillonite was modified by a cationic surfactant [hexadecyltrimethylammonium bromide (HDTMA-MMT)] and used as sorbent to remove bromocresol green (BCG) from aqueous solutions. The effect of several factors such as surfactant loading rate onto the clay, contact time, pH, adsorbent dosage, dye concentration, and ion strength were investigated on the sorption. The equilibrium time for BCG sorption was reached at contact time of 20 minutes. Fitting the experimental data to different kinetic and isotherm models showed that the experimental data are well described by pseudo-second-order kinetic ($R^2 > 0.99$) and Freundlich isotherm ($R^2 > 0.99$) models. According to the results of this study, HDTMA-MMT can be considered as a low-cost, eco-friendly, and highly effective option for the sorption of BCG from aqueous solutions.

KEYWORDS: Azo, Bromocresol Green, Clay, Hexadecyltrimethylammonium Bromide

Date of submission: 14 Sep 2015, ***Date of acceptance:*** 27 Dec 2015

Citation: Omidi-Khaniabadi Y, Jafari A, Jourvand M, Saeedi S, Basiri H, Nourmoradi H, et al. **The study of azo dye removal from liquid medium by modified clay.** J Adv Environ Health Res 2016; 4(1): 9-17.

Introduction

Water pollution due to discharging of industrial effluences into water bodies has been recognized as a serious environmental problem in the world, especially in developing countries.[1-3] The wastewater from industrial processes discharges a large amount of organic and non-biodegradable compounds, including dyestuffs, into the aquatic environment.[4-6] Discharging of colored effluents from industrial activities into water bodies has harmful influence on both human health and aquatic organisms because most synthetic dyestuffs are toxic, carcinogenic, mutagenic, teratogenic, and stable during aerobic degradation.[4,7,8] Azo dyes are the largest group of organic dyestuffs. Due to the high stability of an azo dye in reaction to light, heat, water, and biological degradation even at low concentration, it is very important that it be removed from wastewater before its discharge into aquatic environment.[6,9] bromocresol green (BCG) is an azo dye (anionic) that is generally used as a pH indicator and DNA tracer.[10] It may be harmful to human health and aquatic life. Thus, the removal of BCG from liquid medium is necessary. Several techniques have been examined for the removal of dyes from dyeing effluents such as electrochemical treatment, precipitation, coagulation, solvent

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extraction, biological process, membrane filtration, photocatalysis, and advanced oxidation process.[11-13] Among different methods, adsorption, because of high sorption capacity, high efficiency, and non-toxicity, has been considered to be one of the most frequently used processes for the removal of dyes from colored wastewater.[5] Activated carbon, owing to its high surface area and high uptake capacity, has been commonly applied as an adsorbent to remove different pollutants from aqueous solution; however, it is expensive and difficult to regenerate.[6,14] In addition to activated carbon, various nonconventional and low-cost adsorbents, such as chitosan/bentonite composite,[6] waste rice hulls,[9] Moroccan clay,[13] neem sawdust,[15] fly ash and red mud,[16] diatomite,[17] activated palm ash,[18] organobentonite,[19] eucalyptus bark,[20] smectite-rich clayey rock,[21] and modified kaolin clay and talk,[22] have been used for the removal of dyes from polluted water.

Montmorillonite (MMT) is a natural component, which has been widely applied as sorbent for the removal of many organic pollutants from contaminated water.[5,23] Due to some of its prominent properties, such as low-cost, high surface area, high adsorption capacity, ecosystem friendly, and non-toxicity,[4,5,23] MMT has been considered as a suitable sorbent with high sorption capacity for the uptake of organic pollutants from aqueous solutions. MMT is a type of clay with a hydrophilic nature, so it is necessary that the surface of raw clay be modified by organophilic matter like surfactants.

Modified MMT has been recognized as one of the strongest sorbents among the organo-clays for the removal of pollutants. It has been showed that intercalation of cationic surfactants alters the surface properties of clay from hydrophilic to hydrophobic and intensifies the interlayer basal spacing of the clay.[23] Different researches have been conducted on the sorption of dyes from liquid media using MMT modified by cationic or non-ionic surfactants.[24-28] In the present study, the surface of MMT was modified by the cationic surfactant of hexadecyltrimethylammonium bromide (HDTMA) and was used as adsorbent for the removal of BCG from synthetic wastewater. The effect of different parameters, such as surfactant loading rate, contact time, pH, adsorbent dosage, BCG concentration, and solution ion strength, were investigated on the sorption of dye.

Materials and Methods

The MMT and HDTMA were provided from Laviosa Co., Italy, and Aldrich Co., USA, respectively. BCG was obtained from Alvan Sabet Co., Iran. H_2SO_4, NaOH, and $CaCl_2$ were supplied from Merck Co., Germany. The molecular structure of BCG is presented in figure 1. The stock solution of BCG (1000 mg/l) was prepared by dissolving 1 g of BCG in 1 l deionized water, and the working concentrations were made through dilution of the stock solution.

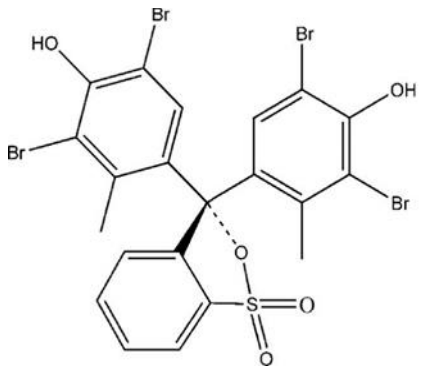

Figure 1. The molecular structure of bromocresol green (BCG)

For the purification of the raw clay, 30 g of MMT was dissolved in 1 l deionized water. A mechanical stirrer (250 rpm) agitated the suspension for 24 hours at room temperature (25 °C) and the solution was then centrifuged (4000 rpm) for 20 minutes. Impurities, such as iron oxide and quartz, due to higher density settled at the bottom of the centrifuge tube. The high purity MMT (located at the upper part of the tube) was subsequently taken, dried at 105 °C, and sieved to less than 125 µm.[23] In order to modify the clay by HDTMA

in the amounts of 20-150 percent of the cation-exchange capacity (CEC) clay, 5 g of high purity clay was separately, introduced in 100 ml deionized water (1:20), and then, mixed with sufficient amount of the cationic surfactant to produce HDTMA-MMT in the surfactant loading rates of 20, 50, 70, 120, and 150% of the CEC clay. The suspensions were agitated by a stirrer (250 rpm) for 24 hours at room temperature. Finally, the HDTMA-MMT was centrifuged (4000 rpm) for 20 minutes, washed (four times with deionized water), dried (60 ^{o}C), and passed through an American Standard Test Sieve Series (ASTM) sieve of 125 µm (mesh No. 120).

Batch adsorption experiments were performed to determine the influence of varying parameters such as surfactant loading rates (20-150 percent of the CEC clay), contact time (0-200 minutes), pH (3-11), adsorbent dosage (1-10 g/l), adsorbate concentration (50-500 mg/l), solution ion strength (25-100 mg/l calcium ions), and temperature (15-45 °C) on the removal of BCG from aqueous solutions. All of the adsorption experiments were conducted at room temperature (except for thermodynamic tests) with 1 g/l HDTMA-MMT in the solution (using 250 ml conical flasks). A mechanical stirrer mixed the suspensions (250 rpm). After the mixing time, the suspensions were centrifuged (3500 rpm) for 20 minutes and the cleared liquid was analyzed by a UV/Vis spectrophotometer. The experiments were duplicated and the average values were applied. The adsorbent capacity (mg/g) for BCG adsorption was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where q_e (mg/g) is the sorption capacity of BCG, C_0 and C_e (mg/l) are the initial and equilibrium dye concentration, and V (l) and m (g) are the solution volume and the adsorbent mass, respectively.[5,13]

Results and Discussion

Effect of the surfactant-loading rate

To reach suitable modification of the MMT clay sample, it is necessary to know the amounts of surfactant that can permeate between the layers of MMT to insure a complete modification.[29] The removal of BCG by HDTMA-MMT with various loading rates of the surfactant (20-150% of the CEC clay) onto the clay is revealed in figure 2. As can be seen, the sorption capacity (q_e) of the modified clay first increased up to 120% of the CEC clay, and then, decreased by increasing the surfactant loading to more than 120% of CEC clay. The higher surfactant loading rates may lead to the complete occupancy of the internal pores of the MMT that will result in the reduction of the diffusion of BCG to these points.[5] The uptake capacity of the HDTMA-MMT in 120% of the CEC clay was 88.02 mg/g. Therefore, the MMT with the surfactant-loading rate of 120% of the sorbent CEC was selected for the next stages of the research.

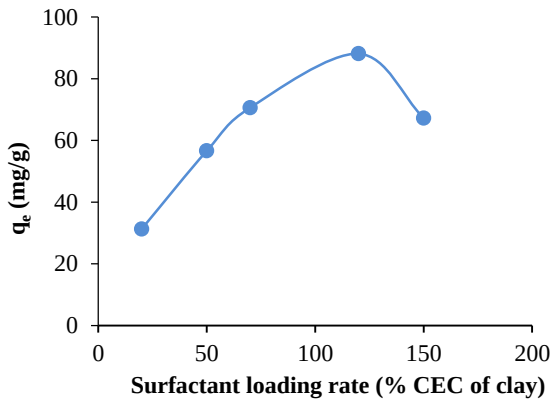

Figure 2. The effect of different loading rates of surfactant on the sorption
Contact time = 24 hours; Bromocresol green (BCG) concentration = 100 mg/l; Adsorbent dosage = 1 g/l; pH = 7

Effect of contact time

The influence of different contact times (0-200 minutes) on the sorption of BCG by HDTMA-MMT at the initial pH was evaluated and the results are illustrated in figure 3(a). As can be seen, a fast initial uptake occurred in the beginning of BCG sorption. Equilibrium was reached at contact time of 20 minutes (q_e = 462.29 mg/g), and then, gradually a fixed state was reached during the remaining contact time up to 200 minutes. The fast sorption of the dyes'

molecules at the beginning of the uptake process time can be due to the obtainability of large numbers of vacant sites on the adsorbent surface by the adsorbate. With increase in contact time, these vacant sites were saturated by BCG and uptake capacity was gradually increased. Therefore, the contact time of 20 minutes was selected as optimum for the subsequent experiments of BCG sorption. Kadhim reported that the equilibrium was observed at contact time of 75 minutes for the removal of BCG by granite,[30] while in this study, contact time of 20 minutes was chosen for the next experiments.

Kinetics study

The investigation of adsorption kinetic models is helpful in understanding the mechanisms of the sorption process. The experimental data were explored via two kinetics models, including pseudo-first order and pseudo-second order, to attain a better understanding of the sorption process (in contact time of 0-200 minutes). The pseudo-first order kinetic model[6,24,31] can be expressed by equation (2):

$$\ln(q_e - q_t) = 1n(q_e) - K_1 t \qquad (2)$$

Where q_e and q_t (mg/g) are the sorption capacities of BCG onto the HDTMA-MMT surface at equilibrium and at any time t (minute), respectively, and K_1 (1/minute) is the rate constant of the pseudo-first order kinetic. K_1 and q_e were determined from linear plotting of $\ln(q_e - q_t)$ against t, which are obtained from the slope and intercept, respectively.

The experiment data of the uptake of BCG was also analyzed by the pseudo-second order kinetic. This adsorption kinetic model can be demonstrate by the following equation.[6,32]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where q_e and q_t (mg/g) are the pseudo-first order kinetic model, and K_2 (g/mg.minute) is the rate constant of the pseudo-second order kinetic. K_2 and q_e were acquired from the intercept and slope of t/q_t versus t, respectively, and are shown in figure 3(b). The different parameters obtained from the pseudo-first order and pseudo-second order kinetic models are presented in table 1. As can be seen, the higher liner correlation coefficient ($R^2 > 0.99$) of the pseudo-second order kinetic shows that the experimental data of BCG sorption are fitted better to the pseudo-second orders kinetic model than other kinetic models described earlier. Moreover, the $q_{e,\ experimental}$ (mg/g) obtained from the experimental data was similar to $q_{e,\ calculated}$ (mg/g) from the pseudo-second order kinetic model. Ghaedi et al. expressed similar kinetic results for the uptake of BCG onto cadmium hydroxide nanowire loaded activated carbon.[6]

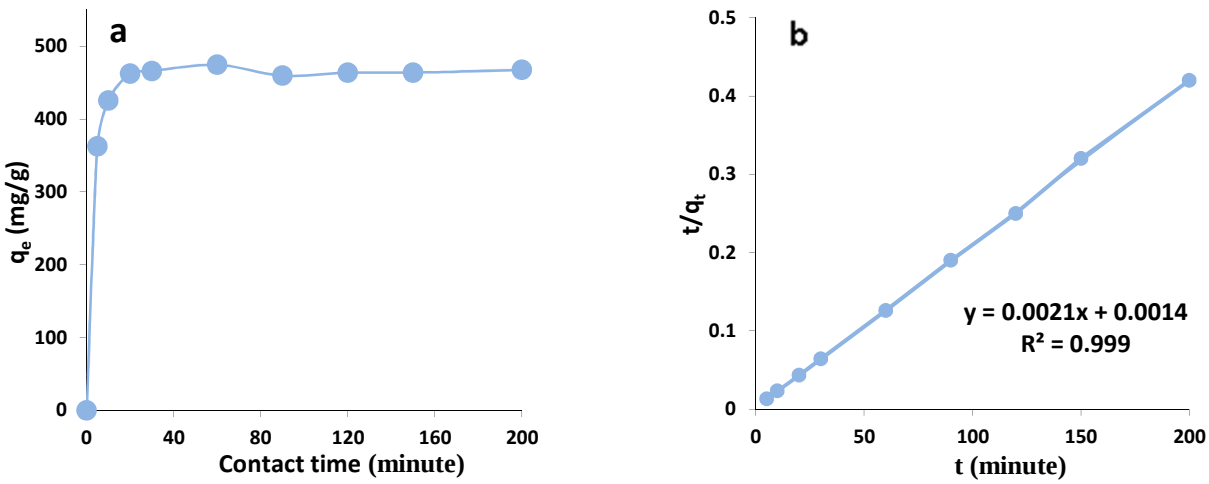

Figure 3. (a) The effect of contact time on sorption [Bromocresol green (BCG) concentration = 500 mg/l, adsorbent dosage = 1g/l, pH = 7] and (b) pseudo-second order kinetic model

Table 1. Parameters of pseudo-first order and pseudo-second order kinetic models in this study

Adsorbate	Pseudo-first order			Pseudo-second order			
	$q_{e,calculated}$ (mg/g)	K_1 (1/minute)	R^2	$q_{e,experimental}$ (mg/g)	$q_{e,calculated}$ (mg/g)	K_2 (g/mg.minute)	R^2
BCG	457	0.12	0.00	462.29	476.19	0.0014	0.98

BCG: Bromocresol green

Effect of solution pH and sorbent dosage

The solution pH influences the surface nature of adsorbent and the level of ionization of adsorbate.[21,33] Moreover, the sorption of adsorbate is affected by the solution pH, because of the sorption of H^+ and OH^- ions in the solution. The influence of solution pH on the sorption capacity of BCG onto HDTMA-MMT surface was investigated over the pH range of 3-11. As can be seen in figure 4(a), the sorption rate of BCG by HDTMA-MMT was decreased with the increasing of the initial pH from 3 to 11 in the solution that concern for the increase in the magnitude of the electrostatic attractions between BCG and positive charge adsorption sites. The maximum sorption capacity (460.15 mg/g) was achieved at a pH of 3. It seems that the sorption of BCG on adsorbent occurred via soft–soft interaction of the functional group of atoms of BCG molecules with soft adsorbent atoms. Dye sorption at higher pH might be due to the formation of OH and subsequent competition with the dye molecules for adsorption sites on the surface of HDTMA-MMT. According to the results of the study by Ghaedi et al., BCG is an anionic dye, so the high sorption of these dyes occur in acidic pH.[6] Thus, pH of 3 was chosen as the optimum pH.

The effect of adsorbent dosages on the sorption of BCG is demonstrated in figure 4(b). It was observed that HDTMA-MMT amounts of more than 1 g/l had no significant effects on the sorption capacity of adsorbent. The sorption capacity of HDTMA-MMT was quickly decreased from 463.71 to 44.8 mg/g with the increase of adsorbent dosage from 1 g/l up to 10 g/l. The decrease in the uptake rate of BCG in the higher dosages of HDTMA-MMT may be due to the lower accessibility of the sorbent active sites resulted from gathering and overlapping of the adsorbent particles. In other words, the phenomenon that occurred in higher content of the sorbent caused a reduction in the dye molecules' sorption onto the HDTMA-MMT. Therefore, the dose of 1 g/l of HDTMA-MMT was selected as the optimum dosage for the remainder of the experiments.

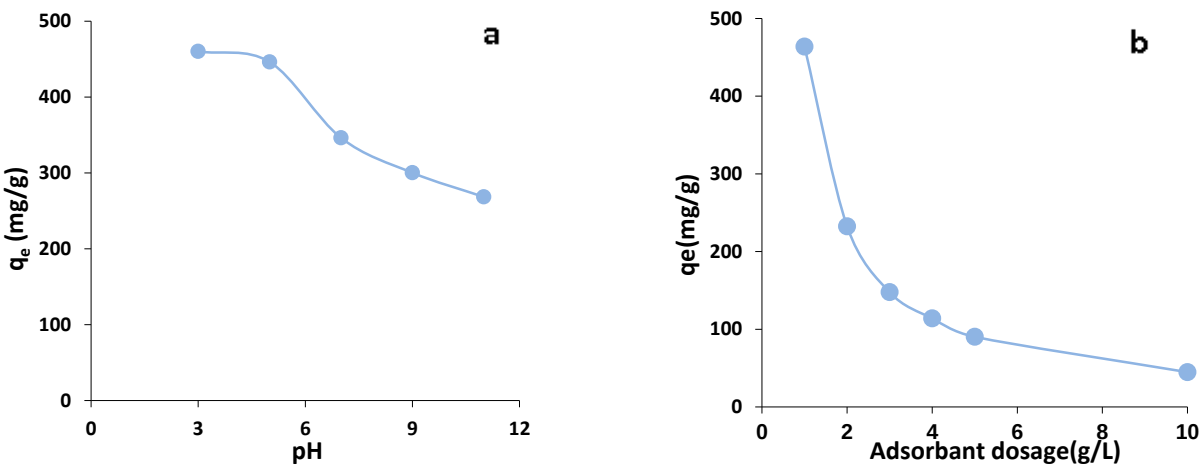

Figure 4. (a) The effect of pH on sorption (contact time = 20 minutes, BCG concentration = 500 mg/l, adsorbent dosage = 1 g/l) and (b) the effect of adsorbent dosage on sorption (contact time = 20 minutes, Bromocresol green (BCG) concentration = 500 mg/l, and solution pH = 3)

Effect of initial dye concentration

The effect of initial BCG concentrations (50-500 mg/l) at solution pH of 3 was investigated and the results are presented in figure 5 (a). As shown, increase in the sorption capacity of BCG is observed by the increase in BCG content from 50 up to 500 mg/l. With the increasing of the initial dye concentration from 50 to 500 mg/l, the amount of BCG adsorbed increased from 36.23 to 468 mg/g. This can be due to the availability of vacant sites on the sorbent surface and increase in the driving force of BCG including van der Waals' force to the active sites of the adsorbent. This state occurs at higher dye concentrations.

Adsorption isotherm

The sorption isotherms are helpful in finding the adsorbate distribution onto the sorbent under the equilibrium condition.[34,35] The results of BCG adsorption were used to determine the adsorption isotherm. Therefore, two isotherms, including the Langmuir and Freundlich models, were employed to this purpose. The Langmuir isotherm approximates the greatest monolayer sorption on the uniform surface of the adsorbent.[6,13,30] The linearized form of the Langmuir isotherm is presented by equation (4):

$$\frac{C_e}{q_e} = \left(\frac{1}{bQ_m}\right) + \frac{C_e}{Q_m} \qquad (4)$$

Where C_e (mg/l) is the equilibrium content of BCG, and q_e (mg/g) is the uptake capacity of HDTMA-MMT during the equilibrium time. The parameters of Q_m (maximum sorption capacity) and b (the Langmuir constant) are achieved from the slope and intercept of liner plotting C_e/q_e versus C_e, respectively.

A dimensionless constant separation factor (R_L) has been used in associated to the Langmuir isotherm model. This parameter is also called the equilibrium factor and is defined by equation (5):

$$R_L = \frac{1}{1+bC_0} \qquad (5)$$

Where b is the Langmuir constant and C_0 the initial dye concentration. The quantity of R_L illustrate if the sorption system is unfavorable (R_L more than 1), liner (R_L equal to 1), irreversible (R_L equal to 0), or favorable (R_L more than 0 and lower than 1). According to the amount of R_L, which is 0.8, the sorption system of BCG on the HDTMA-MMT surface is favorable.

The Freundlich isotherm model is an empirical equation and can be used for non-ideal uptake on the heterogeneous surface of the sorbent.[36] The Freundlich isotherm model can be defined by equation (6):

$$lnq_e = lnK_f + \left(\frac{1}{n}\right) lnC_e \qquad (6)$$

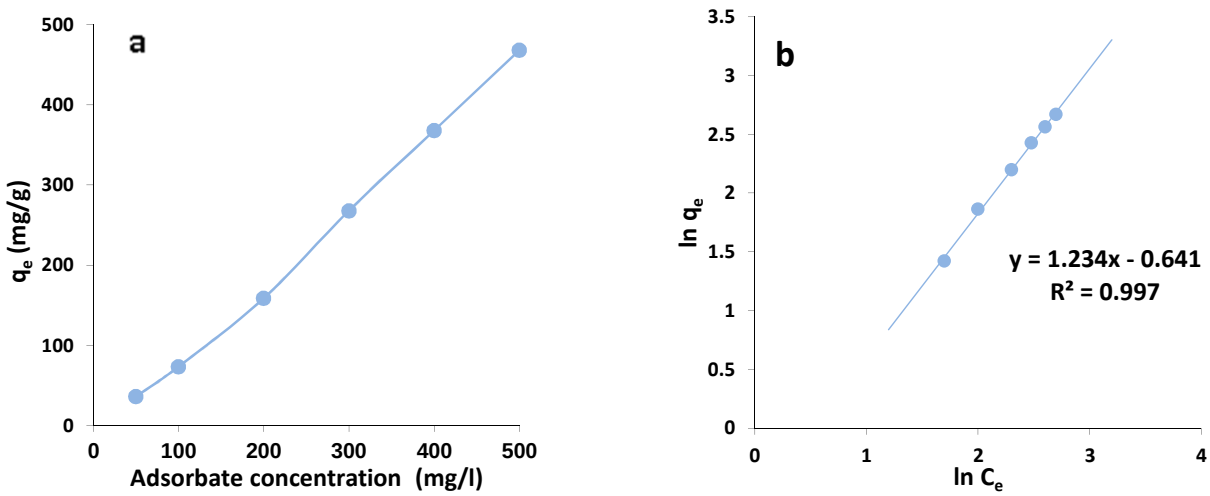

Figure 5. The effect of adsorbate concentration on sorption (contact time = 20 minutes, adsorbent dosage = 1 g/l, and solution pH = 3) and (b) Freundlich isotherm model

Table 2. Parameters of the Langmuir, Freundlich, and Tempkin isotherms

Adsorbate	Langmuir				Freundlich			Tempkin		
	Q_m (mg/g)	b (l/mg)	R^2	R_L	K_f (l/g)	n	R^2	B_l	Kt (l/g)	R^2
BCG	1250	0.0005	0.92	0.82	1.99	1.126	0.99	724.6	3.75	0.88

BCG: Bromocresol green

Where K_f (l/g) and n are constants of the Freundlich isotherm and illustrate the capacity and intensity of the adsorption, respectively. In this isotherm model, n illustrates the sorption intensity.[37] The rates of n of more than 1 show that the uptake bonds between BCG and HDTMA-MMT surface are formatted strongly. The amount of n calculated by the Freundlich model is 1.126, which illustrates that the adsorption bonds between adsorbent and adsorbate are appropriately powerful.

Tempkin assessed the impact of some indirect sorbent/adsorbate interaction on the sorption isotherm. The Tempkin isotherm is illustrated in equation (7):

$$q_t = B_1 lnK_t + B_1 lnC_e \quad (7)$$

Where q_e (mg/g) is the sorption capacity during the equilibrium time, C_e (mg/l) is the equilibrium concentration of BCG, and B_1 and K_1 are constants of the Tempkin isotherm.[10] Amounts of B_1 and K_T were evaluated from the liner plot of q_e against ln C_e. Figure 5 (b) shows the Freundlich isotherm model plot for the sorption of BCG onto HDTMA-MMT. According to the R^2 value presented in table 2, the uptake isotherm model of BCG by HDTMA-MMT is best described by the Freundlich isotherm model. There are some reported similar results for the sorption of BCG from aqueous media onto granite.[30]

Effect of solution ion strength

In the present study, a salt ($CaCl_2$) was used as a model salt to investigate the influence of electrolyte content on the sorption of BCG using HDTMA-MMT. The effect of solution ion strength was evaluated by adding different concentrations of $CaCl_2$ (25-100 mg/l of Ca^{2+} ions) to 100 ml dye solution (100 mg/l) and the results are illustrated in figure 6. As can be seen, the sorption capacity of the HDTMA-MMT in the removal of BCG at the dose of 25 mg/l of Ca^{2+} ions was 468.71 mg/g. Moreover, by increasing of the electrolyte content from 25 to 100 mg/l of Ca^{2+} ions, the sorption amount was decreased from 468.71 mg/g to 432 mg/g. These results may be due to the fact that the active sites of the HDTMA-MMT may be blocked in the greater level of the salt; thus, under this condition, the BCG molecules do not access all active sites of the sorbent surface. This result showed that the presence of salt ions do not have a significant influence on the sorption of BCG via HDTMA-MMT from aqueous solutions. Nourmoradi et al.[23] and Jourvand et al.[5] reported similar results for the removal of pollutants by HDTMA-MMT from aqueous solution.

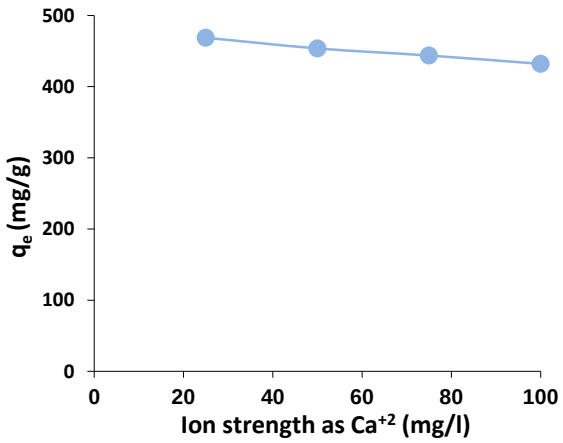

Figure 6. The effect of solution ion strength on sorption [contact time = 20 minutes, bromocresol green (BCG) concentration = 500 mg/l, adsorbent dosage = 1 g/l, and pH = 3]

Comparison with other studies

Table 3 illustrates the adsorption capacities of BCG by several adsorbents. As shown, the uptake capacity [q_e (mg/g)] of HDTMA-MMT, in comparison with other types of sorbents, was higher. Furthermore, the results of literature review on HDTMA-MMT and table 3 showed that HDTMA-MMT also had a greater BCG sorption capability in comparison to many common adsorbents.

Table 3. The comparison of the adsorption capacities of various adsorbents for BCG

Adsorbate	Equilibrium time (minute)	Adsorption capacity (mg/g)	Reference
HDTMA-MMT	20	1250.0	This study
Cd(OH)2-NW-AC	10	108.7	10
Ziziphus nummularia	8	6.2	38
Granite	30	2.1	30

BCG: Bromocresol green; HDTMA-MMT: Hexadecyltrimethylammonium bromide

Conclusion

In this study, HDTMA (as a cationic surfactant) modified MMT (HDTMA-MMT) was used as a cheap sorbent for the removal of BCG from aqueous medium. The influence of various parameters, such as surfactant loading rate, contact time, pH, adsorbent dosage, initial dye concentration, solution ion strength, and temperature, was assessed on dye sorption. The optimum contact time achieved in the sorption process was 20 minutes. Furthermore, the optimum pH obtained was equal to 3. The experimental data were well fitted by the pseudo-second order kinetic and Freundlich isotherm models. The results illustrated that HDTMA-MMT, as a low cost, eco-friendly, non-toxic, and high capacity sorbent towards other sorbents, can be used as an effective option for the sorption of BCG from aqueous media.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

The authors wish to thank the Vice Chancellery for Research at Lorestan University of Medical Sciences and Izeh Branch, Islamic Azad University, Iran.

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