Modified bentonite as adsorbent material for the removal of the basic dye methylene blue from aqueous solutions

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HIGHLIGHTS

• Methylene blue can be successfully adsorbed (96.3%) by 8-hydroxyquinoline modified bentonite in batch design.

• Langmuir and Freundlish models provide information on maximum sorption capacity.

• The maximum adsorption capacity was 526.3 mg.g^{-1} with 100 ppm initial concentration of methylene blue, 120 minutes of contact time, and 0.1 g of modified bentonite sample.

• Modified bentonite has proven to be a promising economic material and recommended for the simultaneous removal of cobalt and methylene blue from aqueous solutions.

GRAPHICAL ABSTRACT
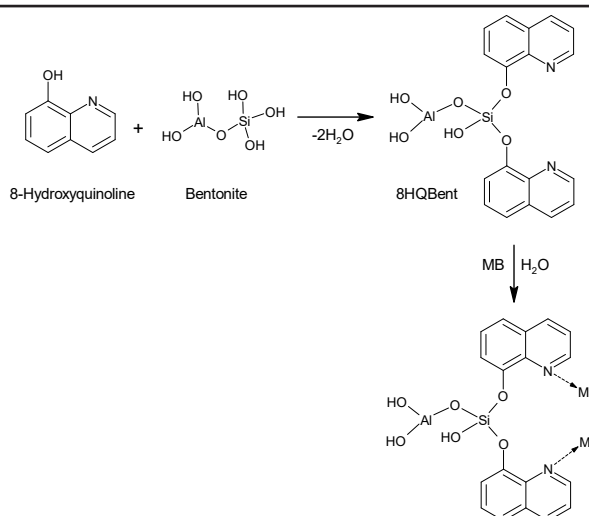
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ABSTRACT

Methylene blue is an organic pollutant found in industrial effluents that is very toxic to humans and the environment. This study used 8-hydroxyquinoline-modified bentonite adsorbent to remove methylene blue from aqueous solutions. In the present work, different doses of modified bentonite were used as a new adsorbent for the removal of methylene blue. The effects of contact time, pH, adsorbent dose, and initial methylene blue concentration were recorded. Then, the adsorption data were described with Langmuir and Freundlich adsorption isotherms. The highest percentage of methylene blue adsorption was observed at pH = 7.5. The optimum amount of adsorbent was 0.1 g.L^{-1} and after 120 minutes, the process reached an equilibrium state. The adsorption of methylene blue increased following an increase in the pH of the solution. It was also observed that the contact time significantly affected the rate of methylene blue adsorption. The experimental data fit much better in the Freundlich ($R^2 = 0.999$) model than the Langmuir ($R^2 = 0.992$) model. So, 8-hydroxyquinoline-modified bentonite has the potential to be utilized for the cost-effective removal of methylene blue from aqueous solutions.

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1. Introduction

With the increasing concern on environmental protection in recent years, the removal of pollutants is gaining public and technological attention. Dyes, which are the main component in the effluent of textile, paper, plastic, food, and cosmetic industries, are an important category of contaminants in water bodies [1,2]. Dyes affect the environment in a number of ways. They are highly visible and possess a high light absorption, which consequently affects the photosynthesis of aquatic plants. Many dyes are toxic and hazardous to aquatic organisms [3]. Dyes can also cause damage to the kidney, reproductive system, liver, central nervous system and cause dysfunction of the brain [4]. The heterocyclic aromatic compound is the chemical structure of the basic dye tetramethylthionine chloride known as Methylene blue (MB) [5]. MB is commonly used for dyeing cotton, wood, and silk. However, MB can cause burns to the eyes resulting in permanent injury to humans and animals [6]. MB can also cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, and tissue necrosis [7]. Consequently, to protect the environment, it is essential to discover effective methods to resolve dye pollution problems before they are discharged [8]. Various conventional methods are used for color removal from dye wastewater, including ozonation, membrane filtration, ion exchange, and activated carbon [9]. Due to the simplicity of design, high decontamination efficiency, and low cost, the adsorption technique is the most effective and attractive process for the treatment of waste water containing dye [10]. Bentonite is an absorbent aluminum phyllosilicate, which is essentially impure clay consisting mostly of montmorillonite [11]. Recently, bentonite clay was successfully employed for the adsorption of metal ions and dyes and has been considered as a potential adsorbent for the removal of pollutants from water [12,13]. The effective application of bentonite for water treatment is limited due to its surface area and the presence of a net negative charge leading to its low adsorption capacity [14]. Modification of bentonite with different materials such as bases, acids, and certain polyhydroxyl cations has been conducted to increase its sorption capacity [11]. Quinolone, a heterocyclic aromatic hydrocarbon whose weakly basic N heteroatom acts as a chelating agent, was used in this study to modify bentonite. The objective of this work was to evaluate the adsorption potential of this modified bentonite for methylene blue. Equilibrium data of adsorption were studied to understand the mechanism of adsorption and the maximum capacity.

2. Materials and methods

2.1. Preparation of adsorbent

The 8-hydroxyquinoline immobilized bentonite (8HQBent) was prepared according to the procedure adopted in [11]. Natural bentonite purchase from Sigma-Aldrich was grounded, sieved, washed, and dried in an oven at 110 °C for 2 h before use. 30 g of bentonite were suspended in deionized water at pH = 4.6; the suspension was mixed with 10 g of 8-hydroxyquinoline to get a loading percent of 25% (ratio 1:3). The mixture was stirred for 48 h to immobilize the 8-hydroxyquinoline onto the bentonite. The 8HQBent solid was separated by filtration, washed three times with deionized water, grounded, sieved, and dried in an oven at 70 °C for 24 h prior to use.

2.2. Preparation of adsorbate

The structure of cationic dye MB used in this paper ($C_{16}H_{18}N_3SCl$, molecular weight is 319.852 ± 0.022 g.mol^{-1}) is shown in Fig. 1 and was purchased from BDH. A stock solution of 1000 ppm was prepared by dissolving 1.0 g of methylene blue in 1 L of distilled water. The MB solutions for adsorption experiments were prepared by diluting the stock solutions to appropriate concentrations. The dye concentrations were estimated by measuring absorbance at 668 nm using a double beam UV–vis spectrophotometer (Spectronic Gyenesys 2). Prior to the measurement, a calibration curve was obtained using standard MB solutions with known concentrations.

2.3. Batch equilibrium studies

The adsorption studies were performed by shaking 0.1 g of adsorbent together with 10 ml of dye solution
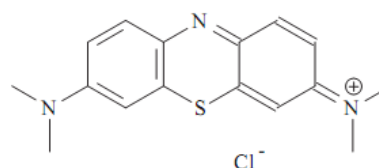

Fig. 1. The chemical structure of methylene blue.

of known concentration and pH in a 50 ml Erlenmeyer flask. The flask was then shaken at 400 rpm at a specific temperature of 25 °C for 2 h. The supernatant liquid portion was withdrawn from the flask and centrifuged at 4000 rpm for 10 min. The pH of the initial dye solution was adjusted with the addition of dilute 0.1 M HCl or 0.1 M NaOH solutions. In the present work, various dye concentrations (100-500 mg.L^{-1}), pH (3-12), and adsorbent dosages (0.01-0.2 g) were used. The removal percent of dye was calculated by the Eq. (1).

Removal (%) = (C$_0$-C$_e$)×100/C$_0$ $\qquad$ (1)

The amount of dye adsorbed onto the adsorbent material (mg.g^{-1}), *q$_e$*, was calculated by the Eq. (2).

q$_e$ = (C$_0$-C$_e$)V / m $\qquad$ (2)

where, *C$_0$* and *C$_e$* (mg.L^{-1}) are the liquid phase concentrations of dye at the initial and equilibrium, respectively, *V* (L) is the volume of the solution, and *m* (g) is the mass of adsorbent used.

2.4. Characteristics analysis

Qualitative and quantitative analyses of inorganic components contained in bentonite were performed using X-ray fluorescence (XRF) (XRF-1500, Shimadzu, Japan).

Scanning electron microscopy (SEM) analysis was carried out for the modified bentonite before and after dye adsorption to study their surface textures. In addition, Fourier transform infrared (FT-IR) analysis was applied on the sample to determine the surface functional groups, using FTIR-2000, PerkinElmer spectrometer, where the spectra were recorded from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Characterization

X-Ray Fluorescence (XRF): The chemical composition of bentonite was determined using XRF analysis and is shown in Table 1. The results indicate that silica and alumina are the major constituents along with some metal oxides such as iron, titanium, magnesium, calcium, and potassium oxides in the form of impurities. Results indicated that silicon, in the form

Table 1. The chemical analysis of bentonite.

Composition	SiO$_2$	Al$_2$O$_3$	TiO$_2$	CaO	Fe$_2$O$_3$	MgO	K$_2$O	MnO
%	57.95	13.51	0.87	6.41	12.97	3.44	4.17	0.19

of bentonite, is the greatest; thus, it is expected that the adsorbate species will be removed mainly by SiO$_2$ and Al$_2$O$_3$. A previous study on 8HQBent by Safa Ozcan *et al*. proved that 8hydroxy quinoline intercalates into the interlayers of natural bentonite [15].

FT-IR analysis of bentonite: Surface functional groups of the adsorbent experienced significant chemical changes during modification. The FT-IR spectra of both bentonite and the bentonite modified with 8-hydroxyquinoline (8HQBent) are shown in Fig. 2. The broad absorption bands observed at 3624 and 3426 cm^{-1} represent the fundamental stretching vibrations of different –OH groups such as Al–OH and OH of water in both bentonite and 8HQBent. In Fig. 2(a), the characteristic band of the –OH group was observed in bentonite at about 1637 cm^{-1}. The bending mode of Al–OH appeared in the region of 914 cm^{-1}. The peaks at 692, 823, and 1039 cm^{-1} were assigned to O–Si–O asymmetric stretching for both materials; the asymmetric bending mode of O–Si–O peak at 467 cm^{-1} as reported in the silicate system [16]. The four observed bands at 1580, 1503, 1382, and 1327 cm^{-1} are characteristic for C–C and C–N ring stretching vibrations [15], in 8HQBent (Fig. 2 (b)), as well as the ring bending vibration obtained at 824 cm^{-1}. These bands are not observed in natural bentonite. This may be considered acceptable evidence for the modification of bentonite with 8-hydroxyquinoline. These spectroscopic results suggest that the introduction of the new functional groups through modification may effectively convert bentonite to a highly adsorbing material.
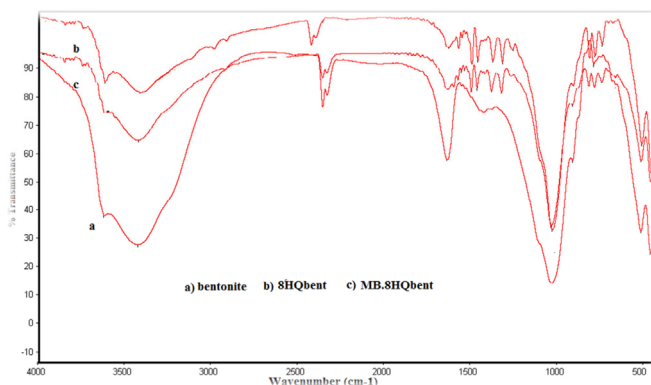

Fig. 2. FT-IR spectra of (a) bentonite, (b) 8HQBent and (c) MB.8HQBent.

Scanning Electron Microscopy (SEM): The surface structure of natural and modified bentonite was analyzed with a magnification of 1000x. Fig. 3 shows the SEM micrographs of bentonite samples before and after modification with 8-hydroxyquinoline. Fig. 3(a) reveals the heterogeneity of particles size distribution in the natural bentonite (the material is composed of irregular shapes). However, Fig. 3(b) shows that the modified bentonite 8HQBent possesses a rough surface morphology with some pores.

3.2. Effect of different parameters on MB removal

3.2.1. Influence of initial adsorbent dosage on dye removal

Adsorbent mass seems to have a great effect on the adsorption process. To investigate the effect of 8HQBent dose on the efficiency of MB removal percentage, adsorption experiments were adopted with
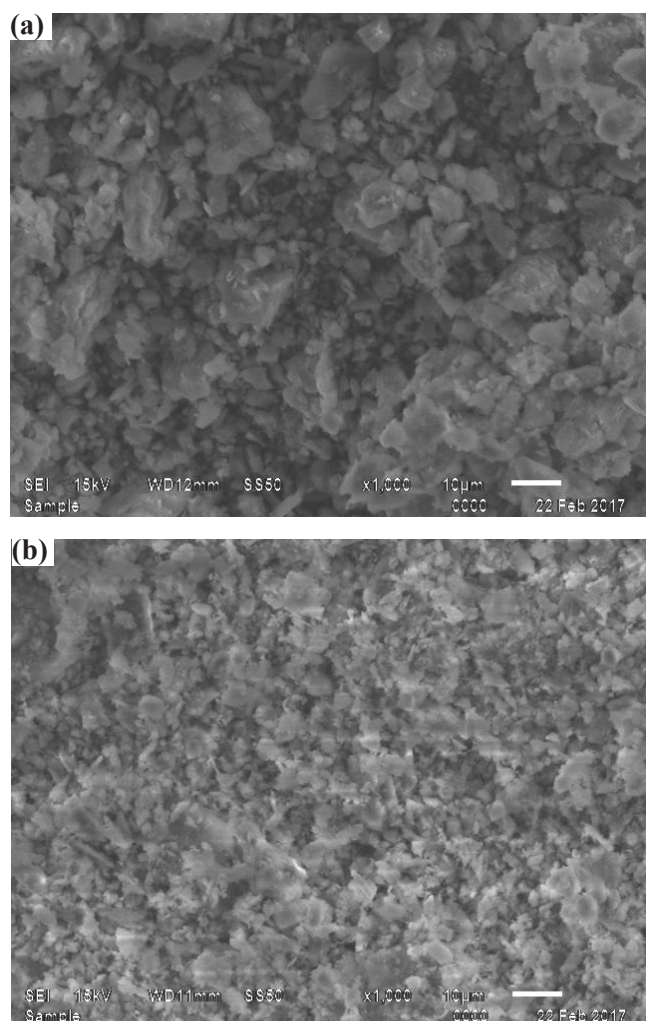

(a)

(b)

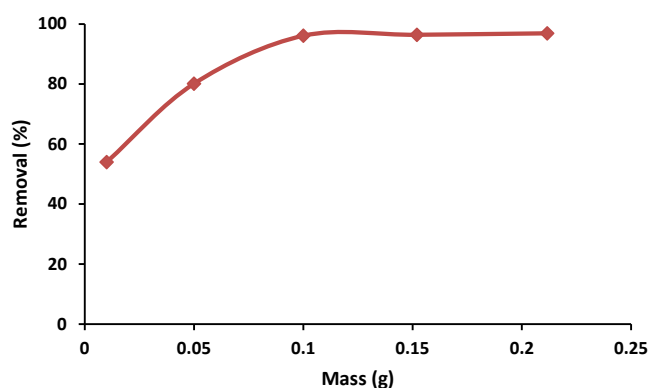**Fig. 3.** SEM images of (a) natural bentonite and (b) 8HQBent.

Fig. 4. Effect of adsorbent dose on adsorption of MB on 8HQBent.

different amounts of 8HQBent ranging between 0.01 and 0.2g. The results are presented in Fig. 4. As can be observed from the graph, increasing the adsorbent dosage increases the percentage removal of methylene blue. There was no drastic increase in the adsorption rate when increasing the dosage of adsorbent beyond 0.1 g of 8HQBent; hence, from an economic point of view, 0.1 g was taken as optimum dosage for removal of methylene blue in the following experiments. The increase of the percentage removal as the adsorbent dose increases can be attributed to the increase in adsorbent active sites for more adsorption of the dye at the fixed 100 ppm. A 96.3% removal rate was attained [17].

3.2.2. Influence of initial pH on dye removal

The pH of the aqueous solutions plays an important role in the whole adsorption process, and in particular in the adsorption capacity. The effect of the solution pH on MB removal on 8HQBent was also investigated in the pH range of 4-11, and the results are presented in Fig. 5. The maximum percentage removal was attained at pH = 7.54. The direct relationship between pH value and methylene blue removal may be caused by the presence of H^+ ions. The reason for choosing these pH values is that from the literature, it was evident that the adsorption of methylene blue was highest in the neutral range. The chemical composition of bentonite is made up of metals oxides with Si, Al, and Fe as the main constituents. These metal oxides form metal hydroxide complexes in the solution. Dissociation of these complexes in an acid or basic medium leads to the development of a negative or positive charge on the bentonite.

Methylene blue is a cationic dye that exists in an aqueous solution as a positively charged ion that, in turn, is influenced by the solution's pH value. A
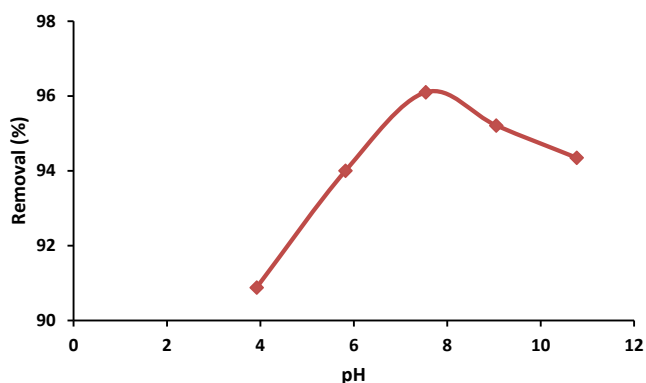
Fig. 5. Effect of solution pH on the adsorption of MB on 8HQBent.

Fig. 6. Effect of the contact time on the adsorption of MB on 8HQBent.

lower removal is observed at an acidic pH value, and this is probably due to the H$^+$ ions competing with the cationic charge of the dye solution for adsorption on activation sites of the modified bentonite. By increasing the pH value, the number of positively charged sites decreases, and the number of negatively charged sites increases. The adsorption of MB on 8HQBent is due to the electrostatic attraction between the negative charge on the adsorbent surface and the positive charge of the MB. The charged dye is attached to the metal oxides of 8HQBent by an ion-exchange mechanism. A similar effect was observed for methylene blue on NaOH-modified rejected tea [18]. The adsorption is affected by the changes in the pH value of the solution because this parameter affects the degree of ionization of the dye and the surface properties of the sorbents.

As a general rule, pH values lower than the point of zero charge (pH$_{pzc}$) result in lower numbers of negatively charged sites of the adsorbent, thereby increasing the number of positively charged sites, which decrease the adsorption capacity of cationic dyes because of the ionic repulsion between the positively charged surface and the cationic dye molecules. At pH values greater than pH$_{pzc}$, the number of negatively charged sites on the surface of the adsorbent increases so that the extent of adsorption of cationic dyes increases due to electrostatic attraction between the negatively charged surface and cationic dye molecules [19]. The pH value for which ΔpH is equal to zero was taken as a pH$_{pzc}$. Therefore, it can be concluded that the 8HQBent surface exhibited positive zeta potential at lower pH values than pH = 7-8 and negative zeta potential at higher pH values. At a lower pH value than pH$_{pzc}$, the presence of the excess of H$^+$ ions in the solution can develop a positive charge on the surface of the adsorbent. Consequently, the electrostatic repulsion increases between the positively
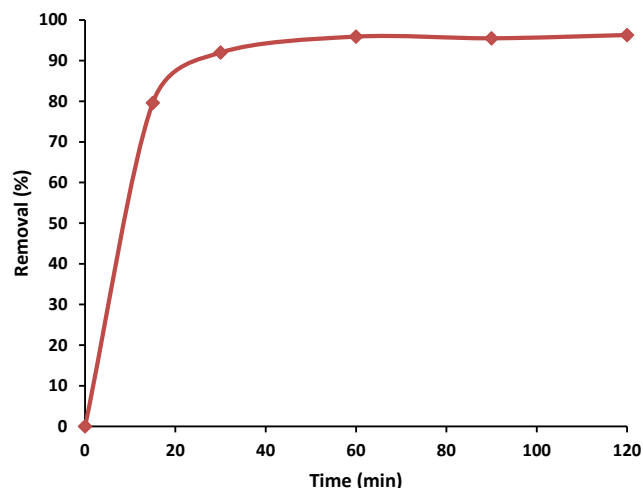
charges of cationic dye MB and the surface adsorbent, which causes a decrease in the adsorption capacity of dye adsorbed. With an increase in pH value, the adsorbent surface became negatively charged due to the deprotonation of the adsorbent surface. The electrostatic attraction between the negatively charged surface and the positively charged cationic dye results in an increase in the sorption removal of the dye. A similar trend has been observed by Amrhar *et al.* [20].

3.2.3. Influence of contact time on dye removal

The dependence of adsorption on contact time was studied using 0.1 g of adsorbent 8HQBent and a 100 ppm methylene blue solution in a fixed volume of 10 ml, see Fig. 6. It is clear that the extent of adsorption is rapid in the initial stages and becomes slower in later stages till saturation occurs. It can be inferred from the rapid sorption rate at the initial stages that there was an abundance of active sites on the external surface of the 8HQBent that resulted in the rapid MB dye removal. After 120 min. the final dye concentration did not vary significantly from the start of the adsorption process. This is basically due to saturation of the active site, which does not allow further adsorption to take place [21]. Therefore, a contact time of 120 min. was used in all the following experiments.

3.2.4. Influence of initial dye concentration on its removal on 8HQBent

The adsorption of methylene blue onto 0.1 g 8HQBent was studied for a 10 ml solution adjusted to pH = 7.54

and containing different MB concentrations. The solutions were shaken for 120 min at room temperature before filtration and measurement of the absorbance. Maximum dye removal at the low initial concentration of methylene blue showed a gradual reduction when the initial concentration of methylene blue was raised. This could be ascribed to a fixed concentration of adsorbent dosage. As the initial dye concentration increases, the adsorption sites are fixed, and saturation is achieved at a low dye concentration. Hence, the higher the dye concentration, the smaller the percentage it can remove [22].

3.3. Adsorption isotherm

The equilibrium isotherms in this study were analyzed using the Langmuir and Freundlich equations (Table 2). The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. A basic assumption is that sorption takes place at specific homogenous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions [23].

$$(C_e/q_e) = (1/q_{max}K_L) + (C_e/q_{max}) \qquad (3)$$

where, q_e is the amount adsorbed at equilibrium (mg. g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg.L^{-1}), and q_{max} (mg.g^{-1}) and K_L is the Langmuir constants reflecting the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of C_e/q_e versus C_e (Fig. 7).

The linear form of the Freundlich isotherm [24] model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption

Table 2. Isotherm parameters for adsorption of MB on 8HQBent.

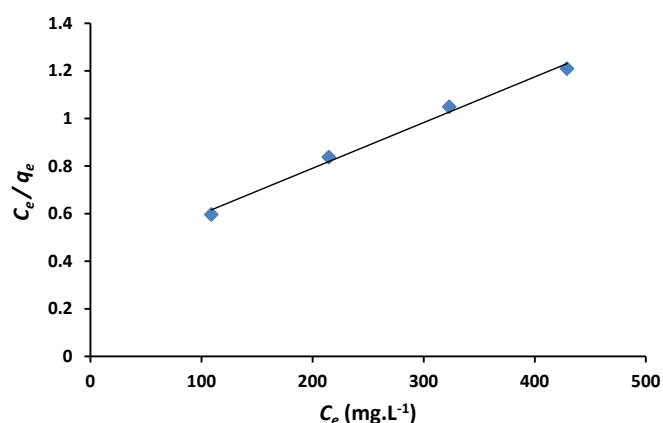| Isotherm model	Calculated sotherm constants
Langmuir	q_{max} = 526.3 mg.g^{-1}
	K_L = 0.005
	R^2 = 0.992
Freundlich	n = 2.08
	K_f = 19.05
	R^2 = 0.996

Fig. 7. Langmuir plot for adsorption of MB on 8HQBent.

over the surface and is expressed by the Eq. (4).

$$logq_e = \frac{1}{n}logC_e + logK_f \qquad (4)$$

where, K_f is the Freundlich constant related to the adsorption capacity while n is constant related to adsorption intensity; in particular, if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process as shown in Fig. 8 [25].

3.4. Interfering of metal ion

Metal dye complexes can be used in textile and tannery industries. Cobalt and methylene blue can be found simultaneously in wastewater from their process. MB and Co are frequently used in analytical research laboratories as redox indicators and consequently may present together in effluents of these laboratories. Thus, we tried to examine the simultaneous removal of both contaminants from aqueous solutions. 0.1 g of 8HQBent was agitated for 2 h with 10 ml aqueous
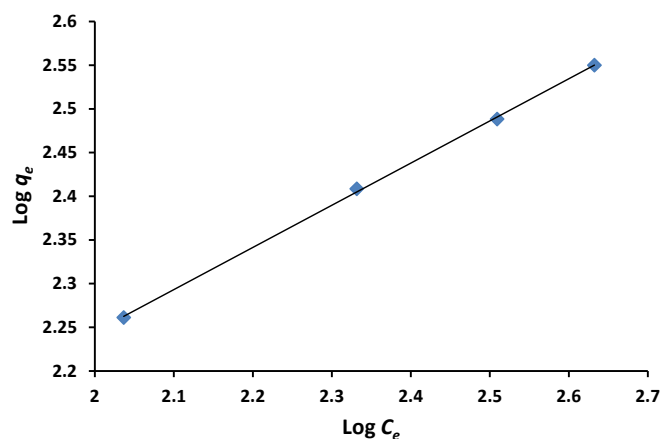

Fig. 8. Freundlich plot for adsorption of MB on 8HQBent.

solutions adjusted at pH = 7.41 containing 150 ppm of Co(II) spiked with ^{60}Co isotope and MB. After equilibration, the percentage removal of Co(II) was assayed by measuring the activity of ^{60}Co before and after equilibration. The capacity of 8HQBent for adsorption of ^{60}Co radionuclide was determined. It was found to be 6.3 mg.g^{-1} for natural bentonite, 10.9 mg.g^{-1} for 8HQBent, and 14.5 mg.g^{-1} for ^{60}Co, while it was 9.6 mg.g^{-1} for MB in a binary solution. The adsorption process increased the adsorbed quantity of the cobalt. The possible interaction mechanism between modified bentonite, methylene blue, and cobalt in a binary system can be interpreted as cobalt or methylene blue having a positive charge that interacts with the silanol-hydroxyl groups of the 8HQBent. Since more than one site is blocked by one molecule, the interaction of cobalt with modified bentonite slows the interaction of methylene blue, and the capacity increases for cobalt adsorption on the 8HQBent. The results indicated that the modification process increases the sorption capacity, and therefore, 8HQBent could be used as an adsorbent material for radionuclide decontamination at the same time as MB solutions (Table 3).

3.5. Adsorption mechanism suggested for MB on 8HQBent

The reaction of natural bentonite with 8-hydroxyquinoline to yield 8HQBent occurs by the silanol groups in bentonite. Examination of 8HQBent as an adsorbent for MB recovery from aqueous solutions was studied. The results indicate the possibility of adsorption of the basic cationic dye MB on 8HQ modified bentonite by suggesting the mechanism as seen in Fig. 9. Three consecutive steps were involved in the removal of dye from water on 8HQBent. First, the adsorbate species migrated from the bulk liquid phase

Table 3. Comparison of sorption capacity of MB on some natural and synthetic sorbents.

Sorbent	Capacity (mg.g^{-1})	Ref.
NaOH rejected tea	242.11	[18]
Peach shell	183.6	[25]
Spent tea leaves	300.05	[26]
Garlic pell	82.6	[27]
Tartaric acid treated bagasse	57.14	[4]
HCl treated saw dust	229.8	[28]
Illitic caly	13.6	[20]
8HQBent	526.3	present work

to the outer surface of the adsorbent particles (film diffusion). Secondly, the dye species moved within the micro- and macro-pores of the adsorbent particles (pore diffusion). Thirdly, the reaction of the adsorbate–adsorbent species took place on the surface.

4. Conclusions

• Chemically modifying bentonite with chelating agent 8-hydroxyquinoline generates a porous surface with a high surface area, which is suitable for the adsorption of basic cationic dyes like methylene blue.

• The results of batch experiments for removal of MB showed that the adsorption capacity increased as the contact time and the initial pH of MB solutions increased, with the maximum adsorption capacity occurring at pH = 7.5. However, the adsorption capacity decreased as the mass of the adsorbent increased.

• The equilibrium experimental data fit the Langmuir and Freundlish isotherm equations. The data better fit the Freundlish equation with regard to the R^2 value.
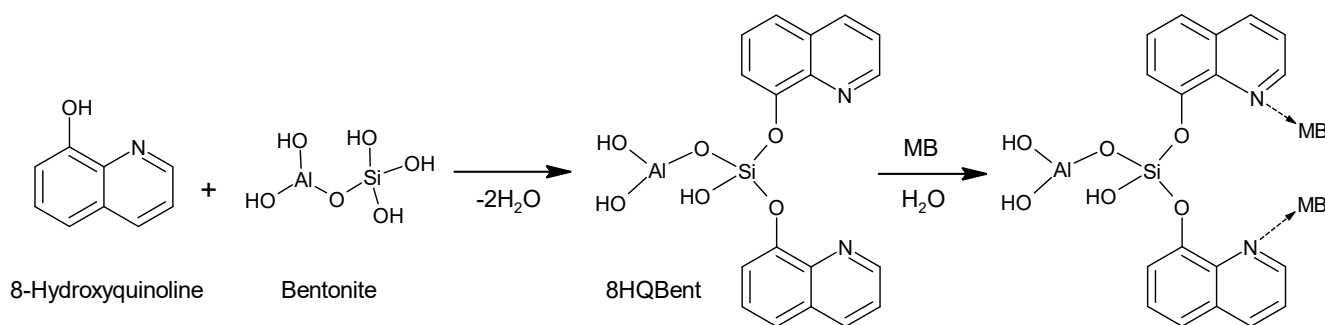

Fig. 9. The possible mechanism for MB adsorption onto 8HQBent.

• Modified bentonite has proven to be a promising economic material and is recommended for the simultaneous removal of cobalt and methylene blue from aqueous solutions.

References

[1] M. Doğan, H. Abak, M. Alkan, Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters, J. Hazard. Mater. 164 (2009) 172-181.

[2] H. Yan, W. Zhang, X. Kan, L. Dong, Z. Jiang, H. Li *et al.*, Sorption of methylene blue by carboxymethyl cellulose and reuse process in a Secondary sorption, Colloid. Surface. A, 380 (2011) 143-151.

[3] A.A.M. Al-Wahbi and H.A.Q. Dammag, Removal of methylene blue from aqueous solutions using yemen bentonite, Diyala J. Eng. Sci. 4 (2011) 30-53.

[4] L. Low, T.T. Teng, N. Moradi, B. Azahari, Studies on the adsorption of methylene bue dye from aqueous solution onto low-cost tartaric acid treated bagasse, APCBEE Procedia, 1 (2012) 103-109.

[5] M. Doğan , M. Alkan, Y. Onager, Adsorption of methylene blue from aqueous solution onto perlite, Water Air Soil Poll. 120 (2000) 229-248.

[6] G. Cheng, L. Sun, L. Jiao, L. Peng, Z. Lei, Y. Wang, J. Lin, Adsorption of methylene blue by residue biochar from co-pyrolysis of dewatered sewage sludge and pine sawdust, Desalin. Water Treat. 51 (2013) 37-41.

[7] W. Zhang, L. Dong, H. Yan, H. Li, Z. Jiang, X. Kan *et al.*, Removal of methylene blue from aqueous solutions by straw based adsorbent in a fixed-bed column, Chem. Eng. J. 173 (2011) 429-436.

[8] M. Khodaie, N. Ghasemi, B. Moradi, M. Rahimi, Removal of methylene blue from wastewater by adsorption onto $ZnCl_2$ zctivated corn husk carbon Equilibrium studies, J. Chem. 2013 (2013) 383985.

[9] M.A. Mohammed, A. Shitu, A. Ibrahim, Removal of methylene blue using low cost adsorbent: A review, Res. J. Chem. Sci. 4 (2014) 91-102.

[10] L.B.L. Lim, N. Priyantha, C.H. Ing, M.K. Dahri, D.T.B. Tennakoon, T. Zehra, M. Suklueng, *Artocarpus odoratissimus* skin as a potential low-cost biosorbent for the removal of methylene blue and methyl violet 2B, Desalin. Water Treat. 53 (2015) 964-975.

[11] S.S. Metwally, R.R. Ayoub, Modification of natural bentonite using a chelating agent for sorption of ^{60}Co radionuclide from aqueous solution, Appl. Clay Sci. 126 (2016) 33-40.

[12] K. Bellir, M. Bencheikh-Lehocine, A-H. Meniai, Removal of methylene blue from aqueous solutions using an acid activated Algerian bentonite: equilibrium and kinetic studies, Int. Renew. Energy Congr. (2010) 360-367.

[13] M.L. Cantuaria, A.F. de Almeida Neto, E.S. Nascimento, M.G.A. Vieira, Adsorption of silver from aqueous solution onto pre-treated bentonite clay: Complete batch system evaluation, J. Clean. Prod. 112 (2016) 1112-1121.

[14] H. Tahir, M. Sultan, Z. Qadir, Physiochemical modification and characterization of bentonite clay and its application for the removal of reactive dyes, Int. J. Chem. 5 (2013) 19-32.

[15] A.S. Ozcan, O. Gök, A. Ozcan, Adsorption of lead(II) ions onto 8-hydroxyquinoline-immobilized bentonite, J. Hazard. Mater. 161 (2009) 499-509.

[16] H.V. Olphen, J.J Fripiat, Data Handbook for Clay Minerals and Other Non-metallic Materials, Pergamon Press, London (1979).

[17] E.C. Kenechukwu, O.J. Nnaemeka, A.C. Oudney, O.U. Emmanuela, O.E. Emmanuel, Equilibrium and thermodynamic studies for adsorption of methylene blue dye onto raw cassava peel (RCP), J. Emerg. Trend. Eng. Appl. Sci. (JETEAS), 7 (2016) 133-142.

[18] N. Nasuha, B.H. Hameed, Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea, Chem, Eng. J. 166 (2011) 783-786.

[19] M. Soni, A.K. Sharma, J.K. Srivastava, J.S. Yadav, Adsorptive removal of methylene blue dye from an aqueous solution using water hyacinth root powder as a low cost adsorbent, Int. J. Chem. Sci. Appl. 3 (2012) 338-345.

[20] O. Amrhar, H. Nassali, M.S. Elyoubi, Adsorption of a cationic dye, methylene blue, onto Moroccan Illitic Clay, J. Mater. Environ. Sci. 6 (2015) 3054-3065.

[21] C. Umpuch, B. Jutarat, Adsorption of organic dyes from aqueous solution by surfactant modified corn straw, Int. J. Chem. Eng. Appl. 4 (2013), 134-139.

[22] S.K. Bajpai, A. Jain, Equilibrium and thermodynamic studies for adsorption of crystal violet onto spent tea leaves, Water¸ 4 (2012) 52-71.

[23] I. Langmuir, The Adsorption of gases on plane surface of glass, mica and platinum, J. Am. Chem.

Soc. 40 (1918) 1361-1403.

[24] H.M.F Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385-470.

[25] S. Marković, A. Stanković, Z. Lopičić, S. Lazarević, M. Stojanović , D. Uskoković, Application of raw peach shell particles for removal of methylene blue, J. Environ. Chem. Eng. 3 (2015) 716-724.

[26] B.H. Hameed, Spent tea leaves: A new non-conventional and low-cost adsorbent for removalof basic dye from aqueous solutions, J. Hazard. Mater.

161 (2009) 753-759.

[27] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Hazard. Mater. 164 (2009) 870-875.

[28] S.M. Kini, M.B. Saidutt, R. Murty, S. Kadoli, Adsorption of basic dye from aqueous solution using HCl treated sawdust (Lagerstroemia microcarp) kinetic, modeling of equilibrium, Int. Res. J. Environ. Sci. 2 (2013) 6-16.