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Effect of Activation Factors on Adsorption of Methylene Blue by Modified Bentonite

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ABSTRACT

The aim of this investigation was to study the relationship between activation factors and adsorption of cationic dye, methylene blue (MB), by activated bentonite. The adsorption index was investigated as a function of acid type, activation temperature and time. A commercial bentonite was selected as a starting material and the effect of activation agent concentration and heat treatment on MB adsorption were determined in a batch setup. The obtained results showed that the adsorption capacity of activated adsorbents by hydrochloric, sulfuric and nitric acids are not only higher than that for untreated bentonite but also this parameter depends on activation condition and acid concentration. The finding results were confirmed by the measurement of the specific surface area of adsorbents with nitrogen adsorption technique, FTIR spectroscopy and X-ray diffraction. Prog. Color Colorants Coat. 6(2013), 97-108. © Institute for Color Science and Technology.

1. Introduction

Recently, the rapid industrialization of countries causes the deterioration of water and soil by effluents containing biodegradable, volatile and recalcitrant organic materials, toxic heavy metal ions, dyes, etc. Dyes are important water pollutants which are generally presented in the effluents of textile and other industries. The high level of productions and extensive use of dyes generate colored wastewater which produces environmental problems. Thus, the removal of dyes from wastewater is important before contact with natural water. The color of effluents is easily detected by human eyes. Some of dyes are stable in nature and it is difficult to tread them by biological degradation. Therefore, it is necessary to treat the colored effluents before discharging into the water. The removal of dye is carried out by physico-chemical techniques such as coagulation, flocculation and adsorption on adsorbents such as activated carbon, silica gel and clays [1-4].

Adsorption techniques are well known methods in removal of organic materials. Due to importance of adsorption on the surface of solid materials in industrial scale, the adsorption of dyes has been extensively studied by investigators [3, 4]. It is essential to understand the role of material in adsorption of dyes. The activated

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carbon is widely used in the adsorption process due to its high capacity for adsorption of organic components [5]. However, due to the high cost and difficulty of regeneration of activated carbon and other adsorbents, the investigation on effective and low cost adsorbents such as clays has been recently increased for removal of cationic dye [6-8]. In spite of active carbon, clays are relatively cheap due to abundant amount in nature. Cationic dye molecules have very high affinity for clay surface. When the solutions containing cationic dyes are added to clay suspensions, those are adsorbed on the surface of particles. The adsorption properties of clays can be related to the layer charge properties [2-4].

The clay minerals such as kaolinite, montmorillonite and illite found in kaolin and bentonite, have effective potential for this purpose [2, 9]. These kinds of clays present high chemical stability, high specific surface area and high adsorption capacity; hence these materials can be used for removal of dyes from effluents. Bentonite is the best known member of clays that contains montmorillonite crystal. The montmorillonite structure is classified as dioctahedral, having two thirds of octahedral sites occupied by trivalent cations. The idealized structural formula for montmorillonite is $M^{+y}\cdot nH_2O(Al_{2y}Mg_y)Si_4O_{10}$ that M is a cation. The negative charge is balanced by cations located between structural units and these cations may be alkali earth ions such as Na^+ or the alkaline metals: Ca^{2+} and Mg^{2+} [10, 11]. When Ca^{2+} cations are exclusively exchange with montmorillonite surface, the clay is known as Ca-montmorillonite. Generally, montmorillonite is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al^{3+} instead of Si^{4+} in the tetrahedral layer and Mg^{2+} instead of Al^{3+} in the octahedral layer results in a net negative surface charge on the bentonite. This charge imbalance is offset by exchangeable cations (Na^+, Ca^{2+}, etc) at the bentonite particle surfaces. The layered structure of the clay expands after wetting. Na^+ and Ca^{2+} are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the bentonite surface [11]. Illite is the second important mineral that can be found in bentonite composition having K^+ ions. The application range of bentonite, depends on the kind and the amount of montmorillonite, other clay minerals and non-clay crystals.

The applications of bentonite in production of selective adsorbents, bleaching earth, catalyst beds, carbonless copy paper and medication depend on the pore structure of montmorillonite. There are three types of pores in bentonite. Empty spaces in a solid that are smaller than 2 nm are called micropores, those between 2 and 50 nm are known as mesopores and those larger than 50 nm are called macropores. Although the micropores and mesopores lie within the particles, the macropores lie between the particles [12-14]. The adsorption capacity of the macrospores is at negligible level compared to that for the microspores and mesopores. Bentonites are the most important among solids that contain natural micro and meso pores. They also, contain a small amount of micropores. The large amount of smectite minerals contained in bentonites is the main source of porosity. The physico-chemical properties of bentonites such as adsorption and catalytic activity depend extensively on the micro and meso pores [15]. In the investigation of porous structures, different procedures such as nitrogen adsorption and mercury porosimetry have been used. The adsorption and desorption of nitrogen on bentonite were studied by Onal et al. [12, 13]. The specific surface area of studied bentonite was determined according to the Brunauer, Emmett and Teller (BET) method by using adsorption data and the pore size distribution curve was plotted by using the desorption data. The specific micro and meso pore volumes were determined by this curve. It was reported that bentonite typically is mesoporous adsorbent.

Activation is a chemical or physical treatment applied to certain type of clay to develop the capacity to adsorb colorant agents and other impurities in oils and solutions. The term of activity denotes the chemical or physico-chemical variations in clay structure to improve specific surface area or external charged layer of solid. Activation of bentonite by acid is an important step for adsorption of some impurities by activated clay [13]. This is called activation process. The activation of bentonite is carried out in a continuous stirred tank reactor at low temperatures between 50 and 100 °C in the presence of activation agents, mostly sulfuric acid [14]. During the reaction, the specific surface area of bentonite increases due to decomposition agglomerated smectite particles. The most significant mechanism in the activation of natural bentonite is cation exchange by H^+ ions. During the activation process, a considerable amount of cations were substituted by hydrogen which increases the specific surface area [16]. These transformations in montmorillonite and illite layers significantly change the cation exchange capacity, chemical and mineralogical characteristics of bentonite.

A number of characteristics determine the efficiency and application area of bentonite. These properties are: adsorption capacity, acid properties, catalytic properties, ion exchange capacity, as well as particle and pore size distributions. The acid treatment, besides leaching cations from octahedral and tetrahedral sheets, dissolves impurities such as calcite and replaces the exchangeable cations with hydrogen ions [17]. The acid treatment also opens the edges of the platelets, which in turn results in considerable increase of the surface area and the pore diameters. Usually, the surface area can be increased by acid treatment [12]. The most important variables affecting the properties of the acid activated bentonite are temperature, treating time, and acid concentration. Other variables are the nature of activation agent and the humidity of the clay. When bentonite is treated with acid, the exchangeable ions are replaced by hydrogen ions. During this process, the crystal structure of the bentonite is altered by the leaching of Al^{+3}, Fe^{+2} and Mg^{+2} ions and the specific surface area and porosity are increased. As the mentioned ions leave the clay mineral structures and activation progresses, specific surface area and specific pore volume increase rapidly, reach a maximum and then diminish. The rise in these factors is a result of unoccupied octahedral and tetrahedral spaces, remaining from the mentioned ions that have left the clay mineral layers. The empty spaces grow and micropores are transformed into mesopores and finally some of mesopores disappear due to decomposition of clay mineral structures, leading to drop in specific surface area and specific pore volume [12].

Cationic dye molecules also have very high affinity for clay surfaces and are readily adsorbed when added to clay suspensions [18]. Many of the aggregation and adsorption properties of clays can be related to the layer charge density. The interaction between modified clays with different layer charges and the cationic dye, MB, in aqueous suspension is related to layer charges. The strong aggregation and distribution of the molecules in the clays with higher layer charge is due to negative sites in the clay surfaces and the different coverage of the clay surfaces. The adsorption mechanism of MB on clay structure can be explained as follows. When MB is added to a clay suspension, the dye molecules readily adsorb on the clay particles. This adsorption occurs initially on the external surfaces so that the local concentration of dye in this area increases considerably, inducing the formation of MB aggregates. As time passes, dye molecules can migrate from the external surfaces to the inter-lamellar region, resulting in the de-aggregation of the aggregates and restoring the monomers.

The capacity of acid-activated bentonite to adsorb the dyes normally used in the textile industry is very high at 20 °C. It can be successfully applied to clean the wastewaters of the dyeing industry. The acid dye molecules have such high affinity for the acid-activated bentonite surface that they are completely adsorbed from dilute solution. The surface charge on the adsorbent and the solution of pH play a significant role, influencing the capacity of an adsorbent toward acid dyes ions. Due to the excess negative charge on particle surface, acid-activated bentonite has a greater capacity to adsorb acid dyes. It was reported that the adsorption kinetics of studied dyes corresponding to treated clay material obeys preferably the pseudo-second-order kinetics which provides the best correlation of the data in most cases [19].

The maximum adsorption capacity of violet dye for magnesium oxide-coated bentonite is higher than that for raw material. The surface properties of bentonite could be improved upon modification of magnesium-oxide. The kinetics of adsorption onto bentonite at different initial concentrations was well described by the pseudo-second-order model. The magnesium oxide-coated bentonite has a significant potential for removing basic dye from wastewater [20].

Benzyltrimethylammonium bentonite is an effective adsorbent for removing acid blue from aqueous solutions and it can be represented as a suitable adsorbent and environmentally clean utilization of wastewater. The adsorption kinetics of dye onto modified bentonite was studied on the basis of the pseudo-first-order, pseudo-second-order and intra-particle kinetic models under several different initial dye concentrations, temperatures and pH. A pseudo-second-order and intra-particle diffusion kinetic models have been developed to predict the rate constants of adsorption and equilibrium adsorption capacities [6].

The natural bentonite may be modified with dodecyltrimethylammonium bromide to improve adsorption capability for removing hydrophobic contaminants from water. Na–bentonite and modified bentonite prepared from low-cost natural material have suitable adsorption capacity for the removal of acid blue from aqueous solution. Modified bentonite showed a higher adsorption capacity than Na–bentonite. Kinetic data of adsorption were well fitted by the pseudo-second-order kinetic model, while the isotherm data were well represented by the Freundlich model [7].

Studies have shown that acid activation by HCl or H_2SO_4 of smectite clays produce good bleaching clays [15, 17, 21]. The decolorizing power of activated clays was shown to be efficient for the vegetable oils.

Though the role of clays for the elimination of cationic dyes from wastewaters has been extensively studied [6-8] but the role of activation conditions on adsorption of these materials is not fundamentally investigated. The aim of this work is to study the effect of acid type, concentration, temperature and time on the adsorption of MB from aqueous solutions by activated clay. The study involves a modification of a commercial bentonite in the presence hydrochloric, sulfuric and nitric acids. The modified adsorbents properties are compared with those of commercial bentonite.

2. Experimental

2.1. Materials and characterizations

The bentonite used in this research has been dry ground to obtain the fine particles, using a laboratory jar mill. The obtained powder was passed through a 230 mesh, 63 μm, standard sieve. The selected material is a commercial product. In all of the experiments, fine-sized bentonite comparable with its counterpart used in industrial practices, was selected as an adsorbent. The chemical analysis of used bentonite, presented in mass percent, was determined by XRF technique (Model S4 Explorer 7KP103, Brucker, Karlsruhe, Germany).

The FTIR spectra were also obtained by Fourier transform infrared spectrometer (Model Unicam Mattson 1000, Philips). The FTIR spectra were recorded in the wave number of 400–4000 cm^{-1} for starting and activated adsorbents.

The mineralogical composition of bentonite and activated clays were identified by XRD diffractometer (Model D8-Advance, Brucker, Karlsruhe, Germany) with a Ni filter and Cu-kα X-ray and the obtained patterns were compared with JCPDS data. The morphology of bentonite was also observed by scanning electron microscopy (SEM, Model EOL.4401, EOL, Oxford, UK).

The specific surface areas of starting and activated powders were obtained from low-temperature nitrogen adsorption isotherms, using a Quantachrome instrument (Model ChemBET3000, FL, USA). Each experiment was repeated two times and the entire experimental procedure was found to give satisfactory reproducible results.

2.2. Activation procedure

In order to evaluate the effect of activation conditions on MB adsorption, the process was carried out a batch setup. For understanding the effect of acid type on activation process, 37 wt.% hydrochloric acid, 98 wt% sulfuric acid, and 65 wt% nitric acid (Merck, Germany) were used. Dry bentonite powder (4 g) and selected acids (0.25, 0.50, 0.75 and 1.00 mol/l) were separately prepared and mixed thoroughly into three-neck flask. The experimental setup consisted of a 500 ml flask equipped with a condenser. A weighed quantity of charges, 4 g of bentonite and 200 ml of acid solutions, were immediately mixed thoroughly in the flask. The above prepared samples were activated at 25, 50, 75, and 98 °C for 15-90 min through 15 min intervals. The flask containing suspension was heated using laboratory heater and temperature was controlled by thermometer. The suspensions were mixed during the activation using a magnetic stirring mixer and vibrating hot plate. The zero time was counted when the suspension temperature reached to the desired temperature. The dead time between mixing and heating the suspensions was less than 1 min. In order to minimize the dead time, the de-ionized water was heated up to process temperature before mixing in flaks. The activated samples were filtered under vacuum and the precipitates were washed with distilled water until they were free from ions and dried at 60 °C in electrical laboratory oven.

2.3. Adsorption evaluation

The maximum MB adsorption was measured according to the following procedure [22]. The chemical formula of MB is $C_{16}H_{18}ClN_3S$ with a corresponding molecular weight of 319.86 g/mol. The MB powder (Merck, 6045, Germany) was used in this study. MB in aqueous solution is dissociated as cationic dye, $C_{16}H_{18}N_3S^+$, which is a large polar organic cation and is adsorbed onto the negatively charged surfaces of clay minerals. Hence, the value of adsorbed MB can be determined. Theoretically, the amount of MB absorbed by given mass of clay depends on the number of negatively charged sites on the clay particle surfaces [22]. The MB solution was prepared by mixing 1.0 g dry powder with 200 ml of de-ionized water. The clay suspension was also obtained by mixing 2 g of oven-dried adsorbent with 30 ml of de-ionized water and the MB solution was added to the suspension in 0.5 ml increments. After mixing the suspension (1 min for each addition of MB), a small drop of about 1 ml, was placed in Fisher brand filter paper P5. MB coats all the mineral surfaces and the end point is obtained when the un-adsorbed MB forms a permanent light blue halo around the clay aggregate spot. The adsorption index can be calculated as follows:

$$R = \frac{V - V_0}{V_0} \quad (1)$$

where R is adsorption index with respect to initial bentonite, V and V_0 the values of MB adsorbed per unit mass of dry activated and starting adsorbents, respectively.

3. Results and discussion

3.1. Characteristics of bentonite

The chemical composition of bentonite obtained by using XRF analysis, given in Table 1, indicates the presence of silica and alumina as major constituents along with traces of sodium, potassium, iron and titanium oxides in the form of impurities. The starting material is characterized by comparable amount of CaO+MgO. The selected adsorbent presents a higher amount of loss of ignition, normally observed in bentonites.

In Figure 1, the X-ray pattern of untreated adsorbent is presented. From the mineralogical viewpoint, clay is constituted of montmorillonite, illite and opal-CT. Identification of montmorillonite, illite and opal-CT were carried out by referring to JCPDS Cards, Nos. 13-0135, 2-0462 and 25-618, respectively. The phases identified from XRD pattern of clay confirm that montmorillonite is the major mineral. Illite and opal-CT are other main crystalline phases obtained on the XRD pattern of bentonite. XRD results combined with XRF analysis show that most of the aluminum is in the form of montmorillonite. The XRD pattern indicates the presence of substantial amount of opal-CT as an impurity in the bulk material. The adsorbent predominantly consists of montmorillonite. The amount of other phases existing in this material, such as calcite, is negligible.

Table 1: Chemical composition of natural bentonite.

Oxides	(wt.%)	Oxides	(wt.%)
SiO_2	72.75	MgO	2.13
Al_2O_3	12.17	Fe_2O_3	0.57
Na_2O	0.28	TiO_2	0.10
K_2O	0.27	SO_3	0.80
CaO	1.48	LOI[a]	9.34

[a] loss on ignition

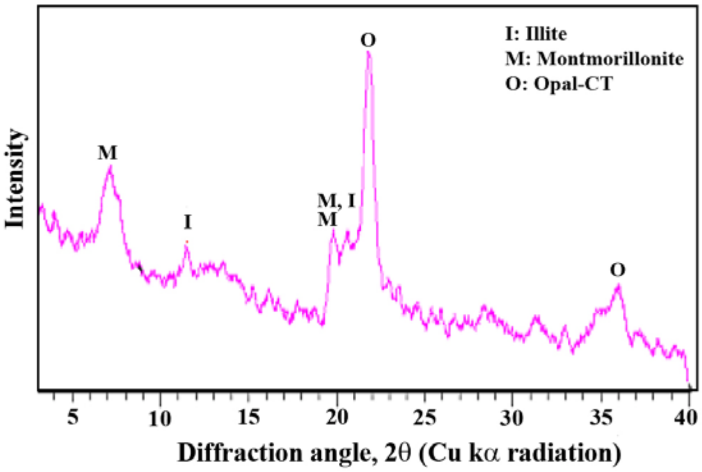

Figure 1: The X-ray pattern of the selected bentonite.

The infrared spectrum of the natural clay, Figure 2, reveals the presence of SiO_2. The band at 798 cm^{-1} can be ascribed to opal-CT which usually has single vibration near 800 cm^{-1}. FTIR spectrum of bentonite is influenced mainly by the nature of the octahedral atoms with which the hydroxyl groups are coordinated. The wide OH band between 3446 and 3670 cm^{-1} is characteristic for this natural adsorbent. The band at 1650 cm^{-1} corresponds to the OH deformation of water. The spectrum of the adsorbent shows intensive band at 1030 cm^{-1} attributed to the Si–O stretching vibrations within the layers, and the vibrations at 520 and 460 cm^{-1} were assigned to Si–O–Al, octahedral, and Si–O–Si bending. The OH bands appear at 920 and 850 cm^{-1} are related to Al_2OH and AlMgOH, respectively [23, 24].

The SEM micrograph of bentonite prepared by milling process is shown in Fig. 3. SEM examination reveals that the natural clay consists of very fine irregular particles. In general, it is difficult to determine their exact texture because of particle coalescence. This sample predominantly consists of small aggregated particles and exhibits a distinct porous structure.

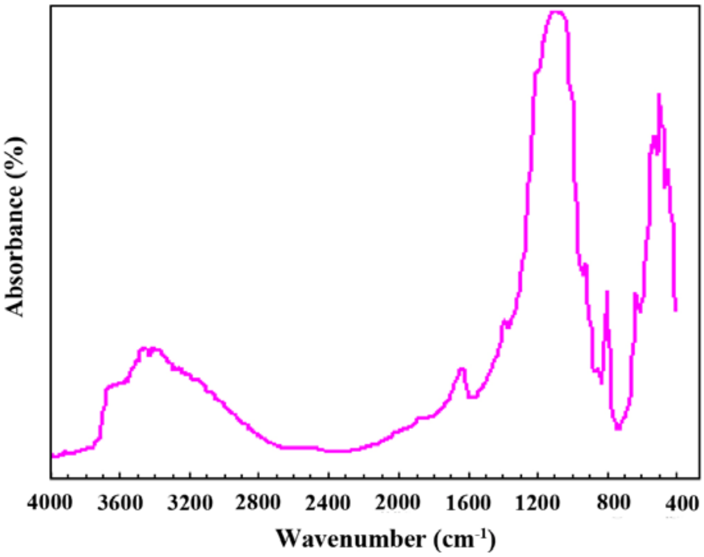

Figure 2: The FTIR spectrum of the selected bentonite.

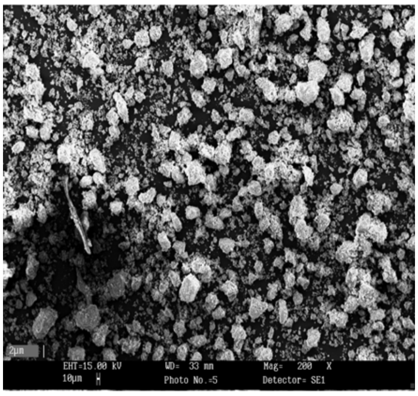

Figure 3: The SEM micrograph of the used bentonite.

3.2. Adsorption of activated adsorbents

Figure 4 indicates the effect of acid concentration on the removal of MB onto activated bentonite from aqueous solution. It is observed that the adsorption is highly dependent on the activation agent concentration which affects the adsorption index. As the acid concentration rises, the adsorption index increases up to a maximum value, then decreases to reach a constant value. As the acid concentration increases from 0.25 to 0.50 mol/l, the exchangeable cations in the montmorillonite and illite structures leave the layers and are replaced by the hydrogen ions [12]. Since Al, Fe, K and Mg rapidly leave the layers, the increment in rate of MB adsorption index is high. As the concentration of acids increases from 0.50 to 1 mol/l, the MB adsorption index reduces to a constant value. This phenomenon shows that the concentration of acid plays important role in the activation process to achieve the maximum adsorption index. The same behavior in the nature of the plots is observed in the presence of different types of acids. It is interesting to note that the maximum MB adsorption index is affected by the acid type.

The activation mechanism of bentonite and the final structure of the acid activated clay can be proposed as follows. The edges of the crystal are opened and the Al^{3+} and Mg^{2+} cations of the octahedral sheet are exposed to the acid and become soluble [12] and the surface pore diameter is expanded. The specific surface area of the bentonite increases to a maximum, and then it reduces by additional treatment [16, 21].

The high adsorption capacity is due to the strong electrostatic interaction between the $C_{16}H_{18}N_3S^+$ and activated bentonite [17]. The maximum MB removal is carried out if the selected adsorbent is activated in the presence of 0.50 mol/l acid. There are limited exchangeable sites on the outer surface of the adsorbent when clay is activated at higher acid concentration; as a result, the adsorption decreases remarkably.

The variations of MB adsorption index versus activation temperature in the presence of different type of acids are shown in Figure 5. The activation process was performed in the presence of 0.5 mol/l acids for 60 min. It is obvious that the MB adsorption increases with the activation temperature, reaching to a maximum value at 98 °C. The activation rate is enhanced when HCl is used. Also, it is interesting to note that the acid type has significant effect on MB adsorption. The maximum value of MB adsorption is obtained in the presence of HNO_3.

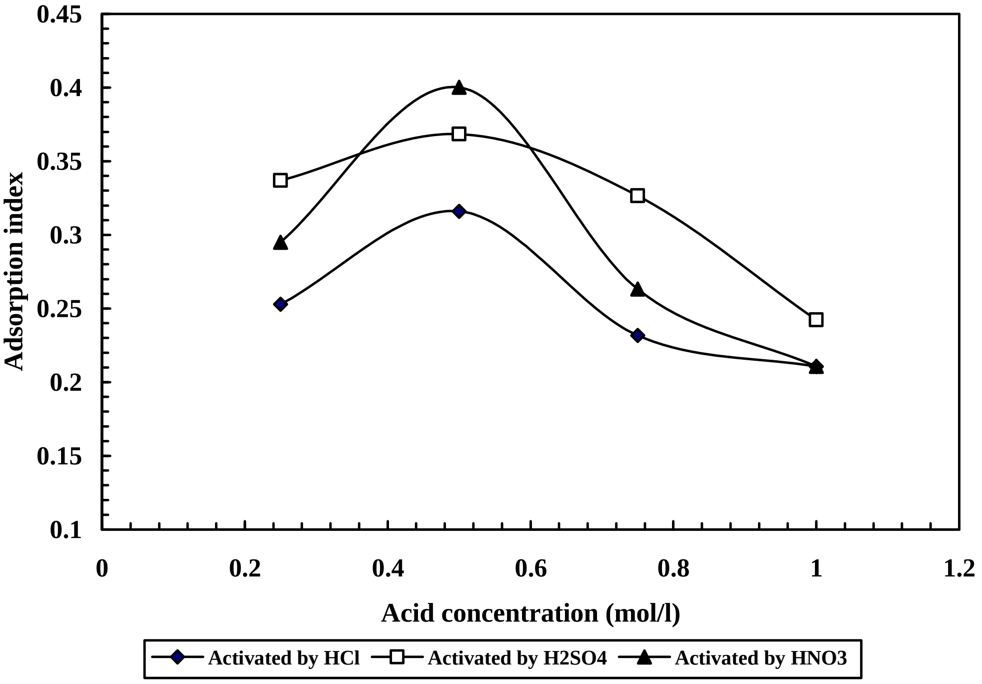

Figure 4: The variation of MB adsorption index of activated adsorbent versus acid concentration.

The effect of activation time on the amount of MB, adsorbed onto bentonite activated in the presence of different acids was also investigated in the range of 15-90 min.The influence of activation time is presented in Figure 6. The activation process was performed in the presence of 0.5 mol/l acids at 98 °C. When the activation time was increased, the adsorption index linearly increased up to maximum values.

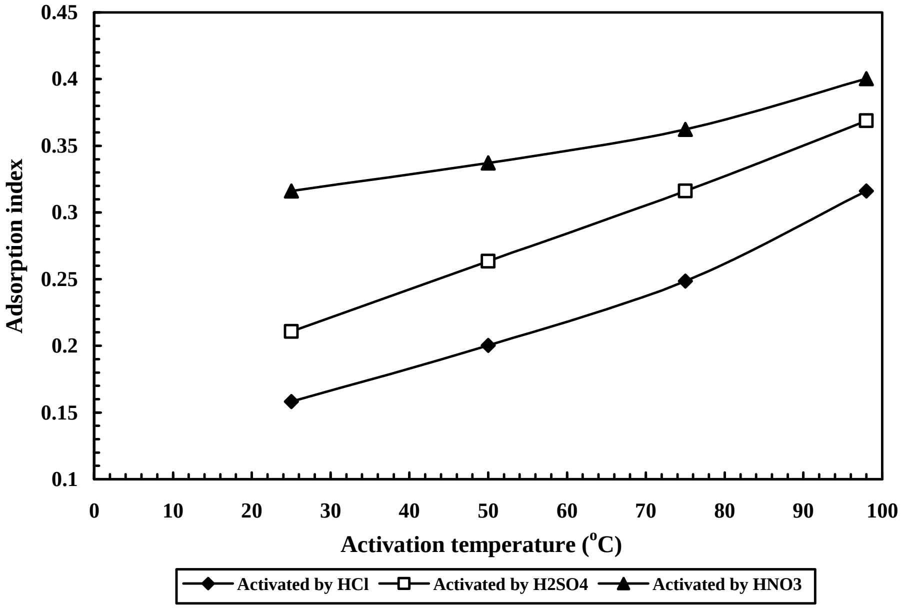

Figure 5: The variation of MB adsorption index of activated adsorbent versus temperature.

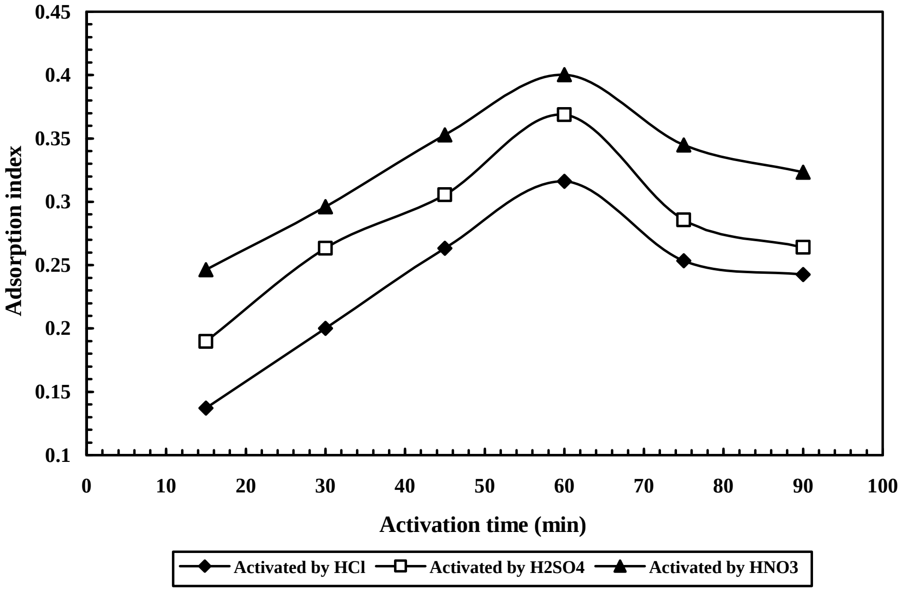

Figure 6: The variation of MB adsorption index of activated adsorbent versus time.

The removal rate of MB onto activated bentonite by adsorption was initially rapid and then rapidly falls down until it attains an equilibrium value, beyond which there was no significant increase in the rate of MB removal. Maximum adsorption index was observed at 60 min. It can be seen that beyond this point, there is further decrease in the adsorption index and it is finally fixed as the equilibrium value. The equilibrium adsorption index of MB onto activated bentonite was also affected by acid type which indicates that the adsorption of MB onto modified adsorbent surface was favored when the clay was activated in the presence of nitric acid.

This is partly due to the attractive forces between MB and bentonite. Based on the above results, it implies that activation time plays a vital role in this system. Before and after optimum activation time, the adsorption index shows different trends at various times. In general, below the optimum points, an increase in the time leads to an increase in dye adsorption rate, which shows a kinetically controlling process. After the optimum condition, the MB uptake decreases with increasing time indicating that the activation time should be controlled to achieve maximum index in the presence of nitric acid.

3.3. Mechanism of MB adsorption

The changes in the FTIR spectra of activated bentonites treated in the presence of 0.5 mol/l acids at 98 °C for 60 min are shown in Fig. 7. The FTIR spectra of the bentonites treated by different acids show the strong bands at 800 and 1030 cm^{-1} attributed to the amorphous silica, Si–O. Also, the vibrations at 1650 cm^{-1} are related to OH deformation of water. The bands at 460 and 520 cm^{-1} assigned to Si-O-Si and Si–O–Al bending vibrations, respectively. The OH bending bands appear at 850 and 920 cm^{-1} are related to AlMgOH and Al_2OH, respectively. The broad band between 3446 and 3670 cm^{-1} corresponds to the vibrations of OH groups which are presented in the clay minerals. In conclusion, no changes in the positions and intensities of the bands were observed. The FTIR spectra indicate that the clay mineral structures are not decomposed by acids if activation is carried out under optimum conditions.

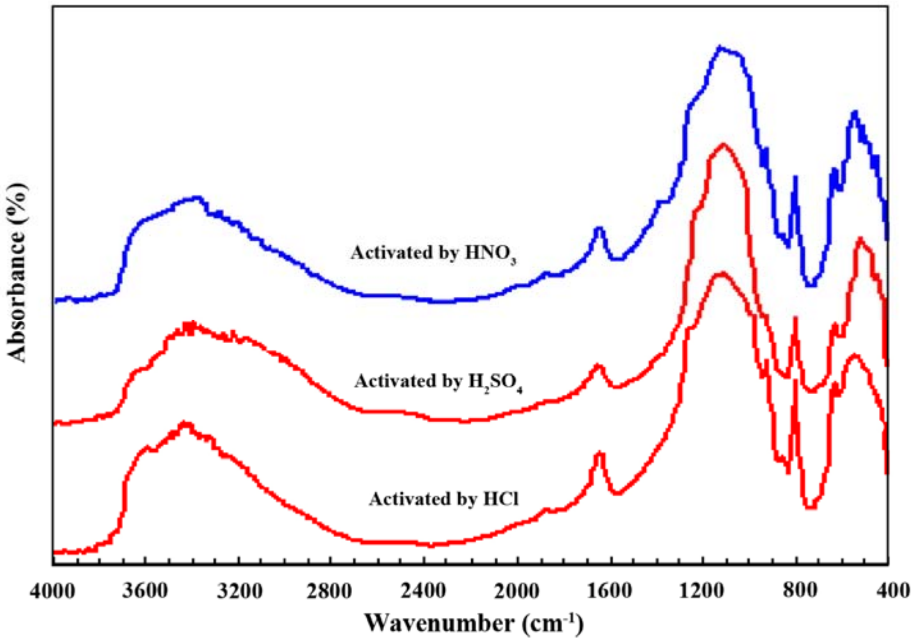

Figure 7: The FTIR spectra of adsorbents activated by 0.5 mol/l acids for 60 min.

The XRD patterns of activated adsorbents which are activated using different types of acids at 98 °C for 60 min are shown in Figure 8. The montmorillonite peak intensity gradually decreases. The illite peaks were disappeared in all of activated adsorbents due to dissolution of potassium from the illite structure in acidic solutions. The intensity of opal-CT approximately is constant for all samples due to its insolubility in acidic solutions. The crystallinity of the clay mineral, as tentatively evaluated by the peak intensity of peaks is reduced. The specific surface areas of untreated bentonite and activated adsorbents are presented in Table 2.

The specific surface area is improved when activation is carried out in the presence of HNO_3. The specific surface area of the sample activated by HNO_3 is two times of that activated by H_2SO_4.The obtained results show that the lowest specific surface area is related to adsorbent activated by HCl. Though, the specific surface area of this adsorbent is higher than untreated bentonite, but this difference is approximately 13 m^2/g. The measured values indicate a very low surface area for untreated bentonite. This phenomenon returns to reactivity of acid with clay crystals. The rise in MB adsorption index is a result of unoccupied octahedron spaces remaining from ions such as Al^{3+}, Fe^{3+}, Mg^{2+}, K^+,. etc that leave the layers of montmorillonite and illite crystals. As the activation progresses, the empty spaces become larger and the micropores are transformed into mesopores [12-14].

Table 2: The specific surface area (m^2/g) of natural and activated bentonites by 0.5 mol/l acid.

Untreated bentonite	Activated by		
3.6	HCl	H_2SO_4	HNO_3
	17.3	21.0	44.3

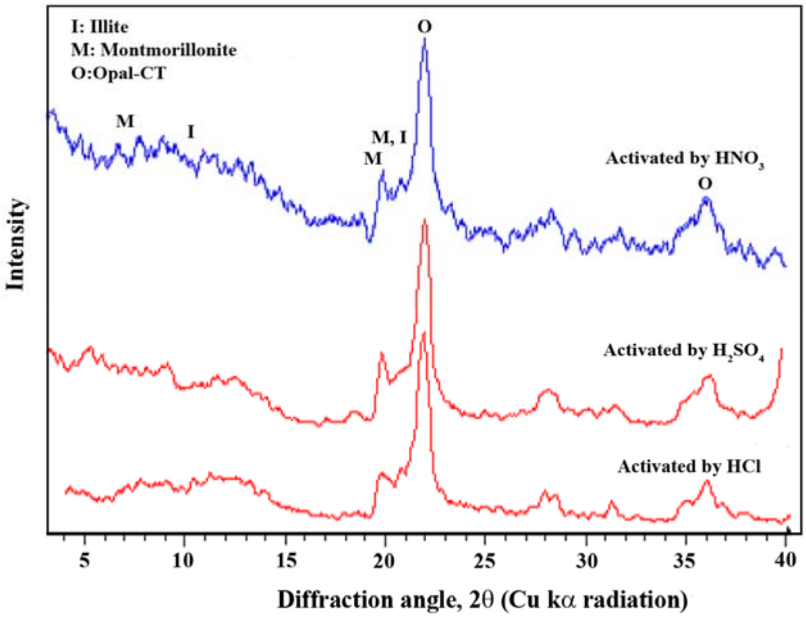

Figure 8: The X-ray patterns of adsorbents activated by 0.5 mol/l acids for 60 min.

Finally, because of the decomposition of crystal structure, some of the mesopores disappear, leading to a drop in MB adsorption. It is obvious that the rate of activation increases by acid reactivity. This factor is the main reason for considerable increase of empty spaces when HNO_3 is used. Therefore, the adsorption of MB is remarkably affected by the acid type.

Expanding 2:1 type layer silicates are especially reactive towards organic materials and polar molecules, because the organic species can enter the interlayer space, forming intercalation complexes. However, large surface area and pore volume play important role in the adsorption capacity of clay minerals. Acid activation of the layered silicate produces variations in the specific surface area, mesopore volume, nature and the number of Lewis and Bronsted surface sites. The increase in surface area and mesopores are *ascribed* to the attacks on some layer edges. This decomposition, which crumbles several layers in the edge region, creates a considerable amount of mesopores. On the other hand, the change in surface properties during acid treatment is ascribed to leaving Al^{3+}, Fe^{3+}, Mg^{2+}, K^+ ions from the octahedral sheet, leading to an increase in number of active sites. This variation in number of mesopores results in increasing the charge in the mesosphere structure. For electrical neutrality, the surface of the layered silicate adsorbs $C_{16}H_{18}N_3S^+$, consequently improving the effectiveness adsorption.

Acid activation of bentonite causes advanced degradation and intensive penetration of acid into grains leading to an increase in the volume of pores. The structural modifications are expected to enhance the adsorption capacity of organic ion. The adsorption is significantly improved with the increment in electrical charge of clay particle surface. It is well known that the contact surface area between the activated adsorbent and $C_{16}H_{18}N_3S^+$ arises with the increment of active sites. The adsorption index is sensitive to the specific surface area; as a result, MB adsorption rises with the increment in interactions between the organic ions and clay particles. In this process, the rate-controlling step can be related to interaction between liquid and solid, because the diffusion of liquid into the clay particles is improved by activation. The following resistances should be considered in adsorption of MB on activated bentonite: (i) diffusion of positive ions from suspension into the film surrounding the clay particles; (ii) diffusion of MB ions from the film onto the negatively charged surface of the clay particles; (iii) adsorption onto solid porous media, and (iv) penetration through the layered silicates and mesopores. In this case some of above resistances are negligible. The resistance (i) and (ii) do not contribute directly to adsorption. Many of the $C_{16}H_{18}N_3S^+$ ions are available around clay particles. The steps (iii) and (iv) are the main resistances controlling the MB adsorption and they weaken by activation in the presence ofnitric acid.

4. Conclusions

The selected natural bentonite is not an effective adsorbent for the removal of methylene blue from aqueous solution. However, natural bentonite may be modified with acid activation in a manner that significantly improves its capability for removing methylene blue from water. The results indicate that activated bentonites by hydrochloric, sulfuric and nitric acids prepared from low cost natural material have suitable adsorption index for the removal of MB from aqueous solution. The adsorbent activated in the presence of 0.50 mol/l showed a higher adsorption index toward MB than those activated by hydrochloric and sulfuric acids under the same conditions. The activation in the presence of nitric acid strongly favors the adsorption index of bentonite powder, reaching maximum specific surface area when it is heated at 98 °C for 60 min. The adsorption index of activated bentonite is negatively affected by the concentration of acid when it exceeds 0.5 mol/l.

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