REMOVAL OF AMOXICILLIN FROM AQUEOUS SOLUTIONS USING MODIFIED BENTONITE

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ABSTRACT

The objective of this study is to modify Iraqi natural bentonite (NB), a readily accessible and low-cost raw material, using various techniques and to explore the possible use of it as an adsorbent for the elimination of amoxicillin (AMX) from aqueous solutions through batch system studies. Chemical and physical processes were used to create the modified bentonite (MB): (1) NB was mixed with cationic surfactants (long and short alkyl chain surfactants), and (2) heat activation created calcined bentonite. The synthesized MB is characterized by surface area, "scanning electron microscopy" (SEM), and "Fourier transform infrared spectroscopy" (FTIR). There are many variables that affect how much AMX is eliminated, such as contact time, pH of solution, rate of agitation, initial concentration, and dose of the sorbent. The results showed that the Freundlich and pseudo-second-order models fit the experimental data better, with maximal removal efficiencies for calcined, long, and short alkyl chain modified natural bentonite being 94%, 70%, and 96%, respectively. The results of the trials showed that the modifications improved NB's capacity to extract AMX from aqueous media.

Keywords: amoxicillin; modified bentonite; sorption; isotherm; kinetic

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ازالة الاموكسيسيلين من المحاليل المائية باستخدام البنتونايت المعدل

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المستخلص

الهدف من هذه الدراسة هو تعديل البنتونايت الطبيعي العراقي كونه مادة خام منخفضة التكلفة ومتوفرة ويمكن الحصول عليها بسهولة، وتم التعديل باستخدام تقنيات مختلفة للتحقق من امكانية استخدامه كمادة مازة لازالة الاموكسيسيلين من المحاليل المائية من خلال دراسات نظام الدفع المتقطع. تم تصنيع البنتونايت المعدل باستخدام طرق كيميائية وفيزيائية: (1) خلط البنتونايت الطبيعي مع المواد الخافضة للتوتر السطحي الموجبة (طويلة وقصيرة سلسلة الالكيل) (2) طريقة التنشيط الحراري لانتاج البنتونايت المعدل حراريا. تم تشخيص البنتونايت المعدل بواسطة المساحة السطحية والمسح المجهري الإلكتروني (SEM) وتحويل فورير الطيفي بالأشعة تحت الحمراء(FTIR) . العديد من المتغيرات تؤثر على كمية الاموكسيسيلين المزال، مثل فترة التلامس، مقياس الاس الهيدروجيني للمحلول، سرعة التحريك، تركيز الملوث الاولي، ومقدار جرعة المادة المازة. أوضحت النتائج أن طرازي(Freundlich) و(pseudo-second-order) تُظهِران مطابقة أفضل للبيانات التجريبية ، مع كفاءات إزالة قصوى للبنتونايت الطبيعي المُعدَّل حراريا والمعدل باستخدام مواد خافضة للتوتر السطحي طويلة وقصيرة السلسلة ،بنسبة 94٪ و 70٪ و 96٪ ، على التوالي . واظهرت نتائج التجارب أن التعديلات عززت قدرة البنتونايت الطبيعي (NB) على استخراج الاموكسيسيلين (AMX) من الوسط المائي.

الكلمات المتاحية: اموكسيسيلين، البنتونايت المعدل، امتزاز، ثبوت درجة الحرارة ،الحركية

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INTRODUCTION

Amoxicillin (AMX) is a broad-spectrum penicillin antibiotic with two major components: an inner-lactam and a side chain known as Dhidroxiphenilglicin. In veterinary pharmacies, gastrointestinal and systemic bacterial infections are frequently treated with it. Prescription medications for humans are frequently prescribed to treat bacterial infections (1, 2). Studies on the antibiotic amoxicillin's adsorption upon bentonite and activated carbon have indeed been done, and the results reveal that this process is crucial. However, pricey activated carbon is the adsorbent that is utilized in this procedure the most frequently. The capacity of bentonite to remove amoxicillin from aqueous solutions has been examined (19). However, due to the hydrophilic nature of clay's mineral surface, amoxicillin adsorption capability was limited. Numerous studies on the features of organoclays have been done as a consequence of their potential to function as good sorbents in removing organic pollutants from groundwater and wastewater (9,24).The goal of this study is to modify natural bentonite using different methods to improve its properties and efficiency to remove amoxicillin from aqueous solutions: The first one is mixing natural bentonite with two cationic surfactants having long and short alkyl chains called cetyltrimethylammonium bromide (CTAB) and tetramethyl ammonium bromide (TMAB), respectively(14).Thermal activation is the second method for modifying bentonite, and it alters the material's physicochemical properties, including its water content, cohesiveness, and specific gravity. The octahedral cation motions inside the octahedral sheet may also be responsible for the dehydration and dehydroxylation processes that happen during bentonite thermal treatment, which increases the material's capacity for adsorption (15,20).

MATERIALS AND METHODS

The State Company of Geological Survey and Mining (Baghdad/Iraq) provided the native bentonite (calcium base) as rock fragments. Bentonite granules size (0.25-0.5) mm were created by crushing these rocks into granules of various sizes after washed them with distilled water, drying them at 90 °C, sieving them using sieves, and repeating the process numerous times. The "State Company of Geological Survey and Mining's laboratories" examined the physical properties and chemical composition of natural bentonite (NB); the results are shown in Table 1. The cationic surfactants utilized were tetramethylammonium bromide (TMAB) and cetyltrimethylammonium bromide (CTAB), which are both short- and long - alkyl chain surfactants. To further imitate the amoxicillin contamination of the water, amoxicillin was used as a contaminant. It was purchased from "The State Enterprise for Drug Industries and Medical Appliances" in Samarah, Iraq (as trihydrate form). The contaminated aqueous solutions were made by dissolving amoxicillin in deionized at a proportion of 0.05 g each per liter to reach (50 mg/L). Without additional purification, all analytical grade reagents were utilized. The original acidity of all of the mixtures was changed by adding HCl or NaOH solution.

Synthesis of modified bentonite (MB)

The Iraqi natural bentonite (NB) was used in this study as a raw material to produce three types of modified bentonite (MB) using two cationic surfactants (CTAB & TMAB) and a thermal process to calcine the NB, these types of MB are symbolized by NB-CTAB, NB-TMAB, and CB, respectively. The first two types of MB (NB-CTAB & NB-TMAB) were prepared by adding (10g) of natural bentonite (NB) to (100mL) of distilled water. The mixture was mixed for 2 hours. Next, weight ratios of the required amount of surface-active agent (CTAB or TMAB) were added of (0.2, 0.25, 0.3, 0.35, 0,4, 0.45, 0.5, 0.55, 0.6 and 0.65 g surfactant/g NB mixture), then the mixing process is continued for 2 hours. The resulting samples (mixtures), called modified bentonite (NB-CTAB & NB-TMAB), which were then cured in an oven at 90°C after being washed many times with deionized water to eliminate excess salts.

Table 1. Characteristics of Natural Iraqi Bentonite

Characteristics	Value
Physical	**0.25-0.5**
Particle size, mm	**6.57**
Moisture content, %	**845**
Bulk density, kg/m^3	**63.5**
Specific surface area, m^2/g	**65**
Cation Exchange Capacity, meq /100g	
Composition (wt.%)	
Silica(SiO_2)	**57**
Aluminum(Al_2O_3)	**13.5**
Ferric oxide(Fe_2O_3)	**4.5**
Magnesium oxide(MgO)	**2.35**
Calcium oxide(CaO)	**8**
Sodium oxide(Na_2O)	**0.7**
Potassium oxide(K_2O)	**0.4**
Titanium oxide(TiO_2)	**0.75**
Loss on ignition(L.O.I)	**12.8**

The (CTAB or TMAB/NB) weight ratio that achieves the maximum amoxicillin removal percent was adopted in the synthesis of the modified bentonite in all subsequent experiments. Another approach was used in this study to produce the third type of MB (CB) through the thermal activation of bentonite to increase its adsorption capacity, dehydroxylation, removal of certain contaminants, and mechanical resistance **(20).** Therefore, the natural bentonite was calcined for 24 hours at 500 °C to produce the calcined bentonite (CB).

BATCH EXPERIMENTS

Under diverse settings, batch experiments were used to study the sorption of amoxicillin (AMX) by synthetically produced modified bentonite. One hundred millliters of amoxicillin solution prepared at a concentration of 50 mg/L was mixed with a preset amount of the MB. An orbital shaker (Edmund Buhler SM25, German) was then used to stir the mixture. Batch studies with different contact times (between 0 and 4 hours), pH of solutions (between 2 and 11), agitation rates (between 0 and 250 rpm), initial amoxicillin concentrations (between 50 and 250 mg/L), and sorbent doses (between 0.05 and 1 g/100 mL) were performed for practical purposes. In order to determine the quantity of amoxicillin that was still present in the solution. A fixed amount of the amoxicillin (AMX) solution was taken out of each beaker and filtered using filter paper (Type “Watman”) to separate the adsorbent from the aqueous solution and then examined by use a double-beam UV spectrophotometer at λ max. = 228 nm. Equation (1) was used to determine the amount of amoxicillin adsorbed onto the modified bentonite **(6):**

$$q_e = \frac{(C_{\circ} - C_e)V}{m} \qquad (1)$$

Where q_e (mg/g) is the amount of drug adsorbed per unit mass of adsorbent, C_o and C_e (mg/L) are the initial and equilibrium concentrations of drug”, respectively. “V (L) is the volume of drug solution and m (g) is the adsorbent mass”. Equation (2) was used to calculate the removal percent (R%) of AMX on MB **(4):**

$$R = \frac{(C_{\circ} - C_e)}{C_{\circ}} \times 100\% \qquad (2)$$

Characterization of modified bentonite

The characteristics of NB and MB (NB-CTAB, NB-TMAB, and CB) have been studied through various analyzes as follows

-**Fourier Transform Infrared Spectroscopy” (FTIR):** Through the use of FTIR analysis, surface functional groups that are present on the sorbent may be identified, which also enables spectrophotometry observation **(18).** Using the KBR pellet method, output waveform in the 400–4000 cm-1 region was carried out with a "Broker Tensor 27" spectrophotometer. It is completed at Tehran University's College of Sciences.

- **Scanning Electron Microscopy (SEM):** By using SEM analysis (NOVA SEM, FEL450L) the structure of the bentonite surface was assessed at a power of ten kV and a current of 6 mA. This flavor demonstrates how the structural characteristics of bentonite have changed both before and after treatment. It is earned at Tehran University's College of Science

- **Surface Area**: When identifying the active sites that contaminants occupy, the surface area is a crucial consideration **(13)**. Using an ASTM D 3663, USA, micrometer to measure nitrogen adsorption at 77 K, a surface area analyzer and the BET technique were used to figure out the specific surface area. It presented a performance at the Tehran University's College of Science.

Isotherm models: Two isothermal models were utilized to characterize the sorption data, as can be seen in the next sections **(16):**

- **Langmuir model:** The “Langmuir isotherm” model is given through the formulation of a monolayer, uniform, and finite adsorption site, which ends up in a saturation value wherein no greater adsorption takes place beyond. It additionally assumes that molecules adsorbed on neighboring sites do not interact with one another as in equation (3)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (3)$$

Where, b is the constant of the free energy of sorption (L/mg), and q_m is the maximum sorption capacity (mg/g), and C_e (mg/L) is the equilibrium concentration of the contaminant in the bulk solution”.

- **Freundlich model:** The Freundlich isotherm can be used to describe adsorption processes on heterogeneous surfaces. This isotherm defines the surface heterogeneity as well as the exponential distribution of active sites and their energy. This model can be represented by the following equation **(7):**

$$q_e = K_F C_e^{1/n} \qquad (4)$$

Where K_F is the intensity of sorption is indicated by the Freundlich sorption coefficient, where n is an empirical coefficient, is (mg/g) (L/mg) $^{1/n}$.

Kinetics study

To comprehend the workings of the drug sorption technique (AMX) in modified bentonite, kinetic sorption models were applied. Pseudo-first order and pseudo-second order are two of these models **(5,11)**:

- **“pseudo-first-order”:** the linear version of this model can be used to compute the sorption rate over time:

$$\ln(q_e - q_t) = \ln(q_e) + k_1 t \qquad (5)$$

Where q_e represents the amount of contamination sorbed at equilibrium (in mg/g), K_1 represents the pseudo-first order adsorption rate constant in (min^{-1}), and q_t represents the amount of contamination sorbed at time t (in mg/g)”.

- **“pseudo-second-order":** Contaminated monolayer must be attached to the sorbent surface, the sorbent must have an equal sorption energy, and the sorbed pollutants must not interact with one another. The model's linear form is represented by equation (6).

Where K_2 is the Pseudo-second-order rate constant (g mg^{-1}.min^{-1}).

RESULTS AND DISCUSSION

Natural Bentonite Modification: At room temperature under specified conditions (time=4 hours, pH=7, agitation speed=200 rpm, C_o=50 mg/L, and dosage=0.5g/100 mL), different samples of modified bentonite (MB) were prepared and tested by combining different quantities of surfactants (CTAB and TMAB) with a specified amount of natural bentonite. The results are shown in Figure (1). It was observed that as the weight ratios (CTAB or TMAB/NB) increases, the AMX removal percentage increases until it reached the highest value of 79% and 48% at 0.5 g CTAB/g NB and 0.6 g TMAB /g NB, respectively, then the removal percent starts to decrease as the ratios of (CTAB or TMAB/NB) increases to reach 75% and 45%, respectively. The decrease in the removal percent can be explained as follows: the presence of the excess amount of cationic surfactants (CTAB or TMAB) on the surface of bentonite leads to increasing the repulsion process between the AMX molecules and cationic surfactants on the surface of MB, which causes a decrease in the percentage of removal. This behavior is caused by the anionic pollutant molecules' electrostatic repulsion to the positively charged modified bentonite surface (12). Therefore, while making the modified bentonite (NB-CTAB & NB-TMAB), which was utilized in all batch experiments in this work, the proportions of (CTAB/NB=0.5) as well as (TMAB/NB=0.6) that produced the maximum removal percent were adopted. For the case of the production of calcined bentonite (CB), firstly, the NB was heated (80-105°C). When NB is heated to these temperatures, water, volatile substances, bacteria, and organic materials are lost. The loss of these elements does not change the structure of the clay. Then, the temperature was raised to between 450 and 500 °C, which caused the loss of hydroxyl and start to change the structure of the bentonite (20). In order to clarify the effectiveness of bentonite modification processes and their impact on increasing the bentonite activity, the CB and NB were tested to use in removing AMX from aqueous solutions under the same conditions that were illustrated in Figure (2). Table 2 displayed the results of this test. As can be seen, employing NB-CTAB, NB-TMAB, and CB boosted the AMX elimination percentage by "6.58, 4, and 6 times" as compared to utilizing NB. This was caused by the bentonite layer's alteration, which raised the layer's spacing and changed the hydrophilic surface of the material into one that was hydrophobic to boost its adsorptive capabilities (21).

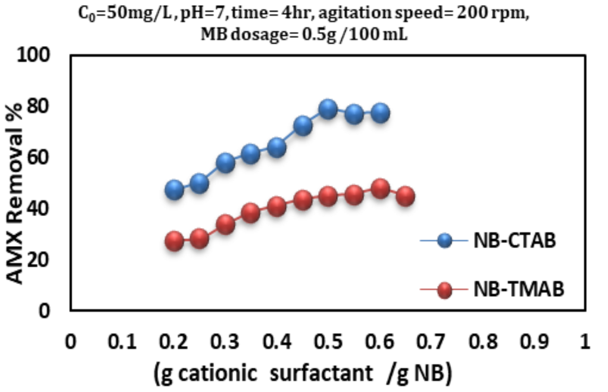


Fig. 1 Effect of CTAB/bentonite and TMAB/bentonite ratio on Amoxicillin adsorption.

Table 2 Comparison of AMX removal by natural and modified bentonite

Impact of operational conditions in batch mode

Contaminant	NB	NB-CTAB	NB-TMAB	CB
AMX	12%	79%	48%	72%

Contact time: The amount of AMX removed by MB using surfactants and the thermal process was studied at different contact times with conditions illustrated in Figure (2). This graph shows that as the contact duration rose, the amount of AMX that was removed increased as well. In addition, the sorption rate was high during the primary stage but gradually decreased after that. It is likely that the fewer MB active sites contributed to the slower sorption. The result shows that at a time (3.5 hours) the maximum AMX removal percent of 79%, 48%, and 70% was achieved for NB-CTAB, NB-TMAB, and CB, respectively. It can be noted that the AMX removal percent for NB-CTAB was higher than NB-TMAB and CB. This outcome can be attributable to the fact that., the adsorption of AMX depended not only on the partition mechanism, but also on the number of hydrocarbon chains within the surfactant molecule that interlayered with NB (22). Since the NB-CTAB has longer hydrocarbon chains and higher surface area, therefore its AMX removal percent was higher than NB-TMAB. Although the CB has a higher surface area than NB-CTAB, it has AMX removal percent lower than NB-CTAB. this behavior can be explained that the NB-CTAB has functional groups due to the presence of CTAB-surfactant that do not present in CB, which lead to an increase in the affinity between AMX and NB-CTAB more than CB.

pH of solution

One of the most important elements influencing adsorption capacity is pH of the AMX solution. This is due to the fact that it affects both the sorbent's surface charge and the quantity of sorbate ionization. In order to test the sorption of AMX using MB at various pH ranges between 2 and 11,. As can be observed, the removal percentage of AMX employing cationic surfactants rose as the pH value climbed up to pH=10, which produced the maximum removal percentages of 86% and 54% for NB-CTAB and NB-TMAB, respectively. After that, the removal percentage seems to have steadied somewhat. This behavior can be explained as follows: when the pH is low, there are too many H+ protons on the adsorbent's active sites, which start competing with the cationic groups of the adsorbate and lower the rate of organic compounds' adsorption; however, when the pH is high, the density of H+ surface charges decrease, which lessens the repulsive forces between the positive electrode adsorbent surface and the adsorbate, increasing the extent of sorption process (17). The results show that in the case of CB, the AMX removal percent increased as the pH value increased until it reached the highest removal percent (82%) at a pH of 6, then the removal percent declined to reach the minimum removal percent (17%) at a pH=11. The AMX is a zwitterionic compound (Pka1=6.71 and pka2=9.41), which has a positive charge at pH values lower than 6.71 (acidic conditions) and a negative charge at pH values higher than 9.41 (basic conditions) compared to the CB, which is primarily composed of montmorillonite with a negative surface charge (5). Therefore, under conditions of this section, with increasing pH values up to 6, the positive charge of the AMX increased leading to the increase in the electrostatic attraction. The percentage of AMX elimination is increased by the negatively charge found on the surface of CB. Then, as pH levels rise, the negatively charged of AMX increases, increasing the repulsive forces with a CB surface since it also has a negative charge, which lowers the AMX removal percentage. This illustrates how the CB behaves at various pH values.

Agitation speed

By varying the speed from “0 to 250 rpm” while keeping the other factors constant, it was possible to determine how much the agitation speed affects the AMX elimination percentage. **Figure (4)** shows that about (20%, 8%, and 14%) of AMX were removed before vibration with NB-CTAB, NB-TMAB and CB, respectively, in addition, the percentage of AMX removal rises with increasing vibration rate until it reaches a higher value of (88%,57 % and 85%) for NB-CTAB, NB-TMAB and CB, respectively. These findings are due to the fact that agitation speed increases the quantity of contaminants that permeate towards the reactive medium's surface. To promote and advance the sorbate to the sorbent sites, appropriate interaction between the sorbate in the solutions and the sites is required **(8).**

Initial concentration

In this set of tests, the effect of AMX concentration values on the removal ratios in the range of 50 to 250 mg/L was studied. In fact, when the initial concentration was raised from 50 to 250 mg/L, the AMX removal percentage dramatically decreased, as seen in **Figure 5**. The overloading of the adsorption (MB) sites with AMX compounds was the primary cause of this decline in removal rates.

MB dosage: The importance of the AMX removal using different MB dosages (0.05-1g/100mL) was investigated, **as seen in Figure (6).** These results demonstrate that only 88%, 83%, and 56% of AMX were eliminated at 0.5 g of NB-CTAB, CB, and NB-TMAB, respectively, when added 100 mL of AMX solution. A considerable improvement in the elimination rate to 97%, 94%, and 68% for NB-CTAB, CB, and NB-TMAB, respectively, may be induced by increasing the MB dose to 0.8 and 0.9 g/100mL for (NB-CTAB & CB) and (NB-TMAB), respectively. This tendency is caused by the fact that as the sorbent (MB) dosage is improved, pore volume, surface area, and the number of open sites available to attach additional AMX molecules all increase. As a result, increasing the MB dosage promotions the elimination percent **(10).** Additionally, it should be noted that an increase in dose that surpasses 0.8 and 0.9 g/100mL for (NB-CTAB & CB) and (NB-TMAB), correspondingly, precludes it from having a significant impact on the AMX removal% due to the stability of the contaminant concentration that stays in the aqueous phase.

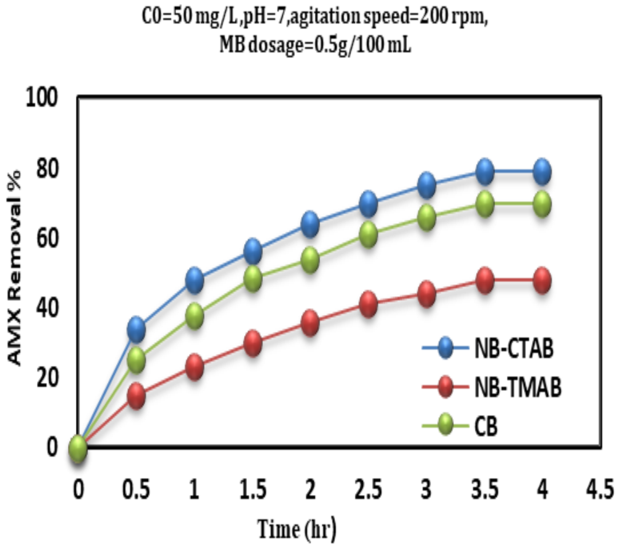


Fig. 2 influence of contact time on the removal percent

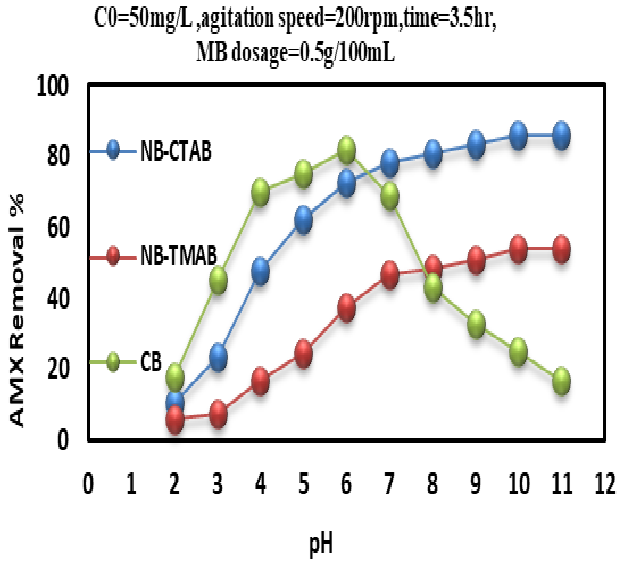


Fig. 3 Impact of solution pH on the removal percent

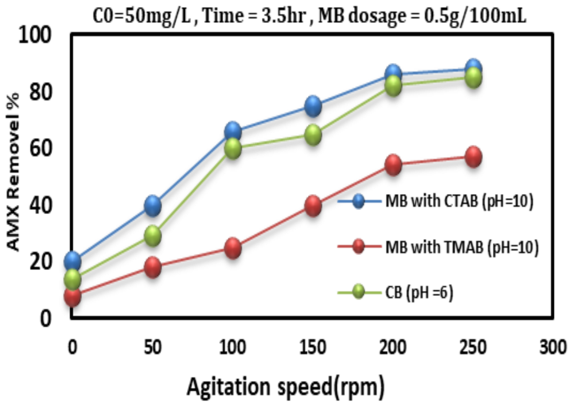


Fig.4 The influence of agitation speed on removal percentage

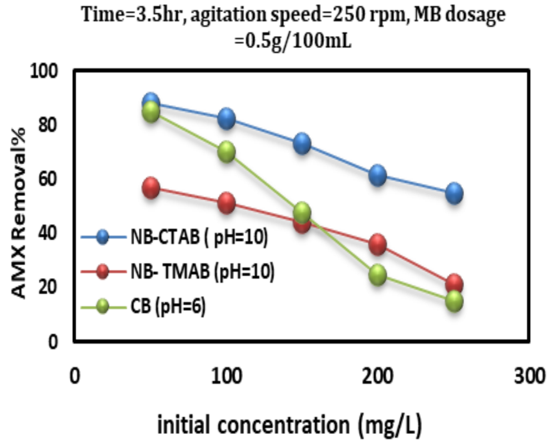


Fig. 5 Effect of initial concentration on the removal percent

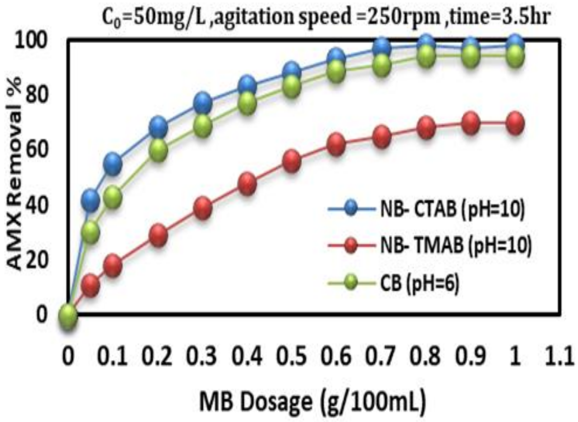
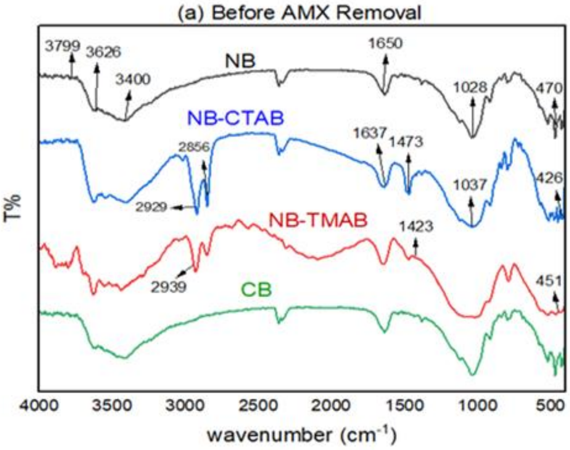
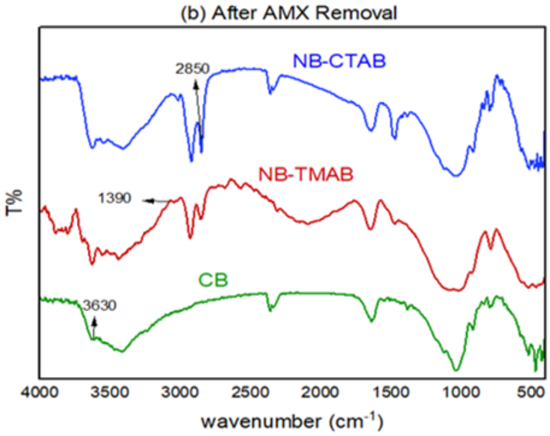


Fig.6 The effect of adsorbent dose on the removal percent

Characterization of reactive materials: “Fourier transform infrared analysis” (FTIR): It is possible to determine the functional groups on the surface that are contained on the adsorbent using FTIR analysis, which also enables spectrophotometric observation. As indicated in Figure (7), these spectra were taken between 400 and 4000 cm^{-1}. It was done this way for NB, NB-CTAB, NB-TMAB, and CB. The strong bands at 1028 and 470 cm^{-1} reflect the Si-O-Si groups of the tetrahedral sheets, while the massive absorption bands at 3799, 3626, and 3400 cm^{-1} on natural bentonite are caused by the O-H bending vibration of the Si-OH (silanol) and Al-OH groups, correspondingly (23). An asymmetric extending phase of Si-O-Si has changed from 1028 to 1037 cm-1 after NB was modified with CTAB (cetyltrimethylammonium bromide). The deformation and trying to bend pattern of Si-O-Si, which was at 470 cm^{-1}, has also changed to 426 cm^{-1}. The presence of C-N vibration in tertiary amines is indicated by the extra peak at 1473 cm^{-1} in NB-CTAB that is not present in NB. The elimination of molecules of water and a modification in the hydrophobicity of natural bentonite are indicated by the maximum absorption of -OH and the bending vibrations of H_2O of NB considerably shifting from a specific rate of 1650 cm^{-1} to a low frequency of 1637 cm^{-1} after being changed with CTAB (13). The asymmetrical CH3 extending maximum absorption and the CH2 scissor vibrational band, which have peaks at 2856 and 2929 cm^{-1} and are sharper than those of the NB, respectively, were determined to be the organic matter in NB-CTAB. The CH3 and CH2 groups illustrate how the CTAB molecules were absorbed into the layers of bentonite minerals. The bentonite clay's surface was altered with CTAB, according to the FTIR readings. After being altered by TMAB (tetramethylammonium bromide), natural bentonite's asymmetries in the Si-O-Si stretching mode changed from 1028 to 1045 cm^{-1}. Along with this alteration, the deformation and bending mode of Si-O-Si has also changed from 470 cm^{-1} to 451 cm^{-1}. Indicating the existence of C-N vibration in TMAB are the extra peaks at 1423 cm^{-1} in NB-TMAB that are present but not in NB (25). Modified bentonite with TMAB produced a less severe peak for organic matter at 2939 cm-1 as contrasted to the MB with CTAB. The symmetrical stretching absorption band for CH3 and the scissor vibration band for CH2 were identified as the sources of these peaks, respectively. The groups CH3 and CH2 demonstrate that the use of TMAB to change the interface of bentonite clay was successfully carried out, and the FTIR data clearly demonstrates that the compounds were successfully incorporated between the layers of bentonite minerals. NB and calcined bentonite were employed to make characterized using FTIR spectroscopy as illustrated in Figure (7). The FTIR spectra of the two types of bentonite—natural and calcined—did not differ significantly. The region of O-H stretching was lessened after thermal activation, as seen in Figure (7). This phenomenon shows that there was less water in the thermal activated bentonite's interlayer. Comparing the FTIR spectra of modified bentonite before and after the sorption of amoxicillin revealed that the peak at 1390 cm^{1-} indicated the existence of -C-N stretching vibration peak and tertiary amine in amoxicillin, whereas the peak at 2850 cm^{-1} showed C-H groups. The change in peak to 3630 cm-1 shows that Amoxicillin binds to the silanol group differently in (NB- TMAB, NB-CTAB, and CB) for each of these compounds (3).





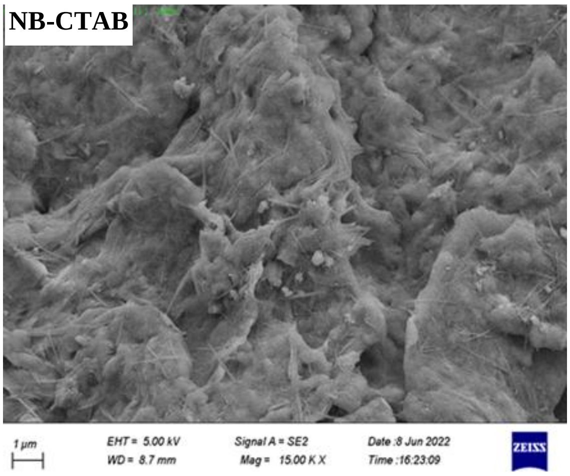
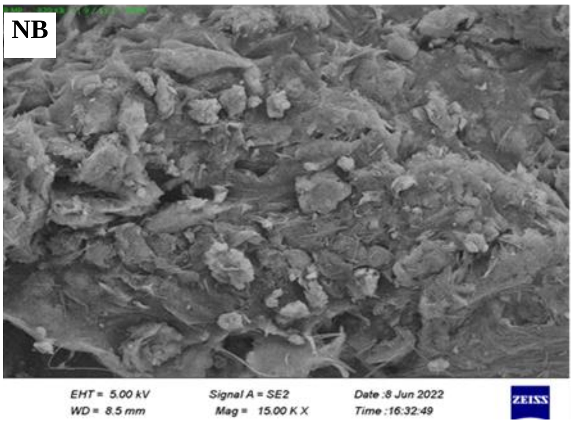


Fig. 7 FTIR spectra for NB and MB

“Scanning electron microscopy” (SEM)

The surface appearance and composition of NB before and after processing were depicted using SEM inspection as shown in Figure (8). As can be observed in this image, the modification had a significant impact on the surface appearance of the NB. It is clear that NB has a pore structure, a rougher and uneven appearance, and a scattered block structure with varying block sizes, whereas NB-CTAB and NB-TMAB have smooth surfaces with a few holes. The fact that the surfactants (CTAB and TMAB) have largely coated the surface of the NB suggests that this fluffy look is caused by a decrease in some of the amorphous phases that were originally connected to the bentonite. The thermal modification of NB can result in a more porous structure compared to raw bentonite because the interlayer gaps have collapsed, creating a more densely bonded structure, according to the SEM picture of the CB.



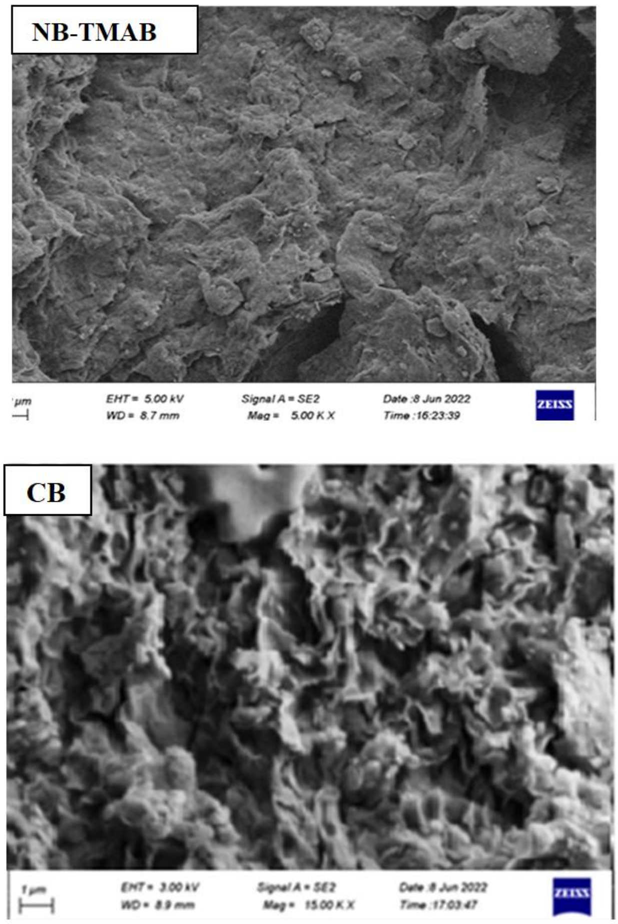


Fig. 8 SEM images of NB and MB

-Surface area: A key determinant of an adsorbent's capacity for adsorption is its specific surface area. A smaller surface area was found in the MB utilizing surfactants than in the NB, according to the test's findings. Surface area for NB was 46.22 m2/g; for MB, it was 23.34 m^2/g and 5.17 m^2/g, respectively (NB-CTAB and TMAB, respectively). This outcome can be attributable to the NB's aggregation characteristics upon surfactant modification. In addition, the organic surfactant molecules entered the NB interlayers and covered its surface, blocking the route between the layers and reducing the pore volume and surface area. This outcome was consistent with several researchers' findings, including those of (8,10,13). The outcomes in the instance of CB demonstrated that the surface qualities of unprocessed bentonite were enhanced by the heat activation of NB. Because the water molecules and volatile chemical substances that stick to the surface of bentonite were removed using heat, the surface area of CB was 72.37 m^2/g, which would have been bigger than that of NB. This indicates that CB has a more porous structure than raw bentonite (15).

Sorption isotherms: Langmuir and Freundlich are two isotherm models that were utilized to complement the experimental results from the adsorption mechanism. Given this, the slope and intercept of the plotted graph were calculated in Microsoft Excel 2016 to obtain the empirical coefficients for each model. **Table 3** listed the values of the calculation parameters and isotherm model constant values. The Freundlich model explicitly yielded a bigger value for the determination coefficient (R^2) in comparison to the Langmuir model, making it better suited to represent the sorption data of AMX.

Sorption kinetics: The pseudo-first and second-order models were used to correlate the data from the kinetics. For the linear plot of the pseudo first and second -order models, plot ln (q_e-q_t) and t/q_t vs t. The constants for these models were derived using the Microsoft Excel 2016 application based on the slop and the y-axis intercept of the straight line. Table 4 lists the values of the kinetic model constants and the coefficients of determination. The fact that the (experimental) value of q_e was closer to the (computed) q_e of the second-order model than the first-order model makes it evident that the uptake of AMX by MB is most likely second-order, regardless of the quantity of R^2. These findings indicate a high prevalence of chemisorption, and this result is considered to be as conclusions of other researchers such as (12,17).

Table 3 Sorption Isotherm Constants for AMX using MB with Coefficients of Determination

MODEL	Parameter	NB-CTAB	NB-TMAB	CB
Langmuir	q_m (mg/g)	21.8818	13.7362	22.1238
	b(L/mg)	0.1453	0.0307	0.0827
	R^2	0.8576	0.9511	0.896
Freundlich	K_F(mg/g)(L/mg)	4.6641	0.9380	2.9736
	n	2.4783	1.7452	1.9557
	R^2	0.9123	0.958	0.9653

Table 4 Shows The Parameters of Kinetic Models and Coefficients of Determination

Model	Parameter	NB-CTAB	NB-TMAB	CB
Pseudo- first - order	$K1(min.^{-1})$	1.32	1.0743	1.1729
	q_e(experimental,(mg/g))	7.9	4.8	7
	q_e (calculated,(mg/g))	13.73	7.75	11.14
	R^2	0.8619	0.9197	0.9249
Pseudo- second- order	K_2 (mg /g .min.)	0.0014	0.00099	0.00106
	q_e(experimental,(mg/g))	7.9	4.8	7
	q_e (calculated,(mg/g))	10.22	7.61	9.99
	R^2	0.9945	0.9922	0.9982

CONCLUSION

The following inferences can be made based on the outcomes of the batch experiments:

In this study, Iraqi natural bentonite (NB) was modified using two cationic surfactants (CTAB and TMAB) and a thermal process as an additional method of modification to create three types of modified bentonite: NB-CTAB, NB-TMAB, and CB. These modified bentonites were used as reactive materials for the batch-mode removal of AMX from aqueous solutions.

- The optimal ratio of (CTAB and TMAB)/NB that resulted in the highest AMX removal percent was 0.5g CTAB/g NB and 0.6g TMAB/g NB that increased the efficiency of the natural bentonite to about 6.5 and 4 times.

-The initial AMX concentration, contact time, initial solution pH, agitation speed, and MB dose were variables impacting the AMX removal process. These parameters were examined in batch mode. The optimized parameters for these variables were 3.5 hours, 10, 6, 10, and 250 rpm, 50 mg/L, 0.7, 0.9, and 0.8 g/100 mL, which, respectively, provided maximum removal efficiencies of 96%, 70%, and 94% for NB-CTAB, NB-TMAB, and CB.

-According to the experimental results, the Freundlich isotherm model can satisfactorily explanation for the MB sorption data (NB-CTAB, NB-TMAB, and CB) with an R^2 of at least 0.9123.

-The results of the sorption kinetics show that the pseudo-second-order model more closely captured the experimental data, indicating that chemisorption was the predominant mechanism.

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