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Ultrasound-assisted removal of methylene blue from aqueous solution by milk thistle seed

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ABSTRACT

The milk thistle seeds were tested as a possible adsorbent for the removal of methylene blue (MB) from aqueous solutions in the absence and presence of ultrasound. Batch adsorption studies were conducted to study the effects of different parameters such as adsorbent dose, initial dye concentration and ultrasonic power on MB dye adsorption. The simultaneous association of ultrasound and stirring leads to an intensification of the adsorption process. The amount of MB dye adsorption with the assistance of ultrasound was improved with the increase of adsorbate initial concentration and with the decrease of adsorbent dosage. The acoustic power was an important factor for the enhancement of the removal of MB dye. Adsorption isothermal data could be well simulated by Freundlich model, and then Langmuir and Temkin models. Langmuir simulation showed that the monolayer adsorption capacities of milk thistle seed were 44.25 and 181.49 mg g^{-1} for the conventional method and for the combined method, respectively. The combination of ultrasound and stirring for the adsorption process was shown to be of interest for the treatment of wastewaters contaminated with MB.

Keywords: Ultrasound; Adsorption; Methylene blue; Milk thistle seed

1. Introduction

Many industries often use synthetic dyes to colour their products including textile dyeing and colouring paper and wool. Over 7×10^5 tons of these dyes are produced annually worldwide. It is estimated that 10–15% of these chemical compounds are discharged into waste streams by the textile industry. Some dyestuffs, among them methylene blue (MB), are not strongly hazardous, but an acute exposure could make them harmful to fish and other aquatic organisms [1]. Furthermore, their presence in aquatic systems, even at low concentrations, is highly visible, reduces light penetration and has a derogatory effect on photosynthesis [2]. Therefore, decolourisation of dye-containing effluent is becoming an obligation both environmentally and for water re-use.

MB is selected as a model compound in order to evaluate the capacity of adsorbents for the removal of dye from its aqueous solutions. MB dye has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools and coating for paper stock.

The removal of color from dye bearing effluents is one of the major problems due to the difficulty in treating such wastewaters by conventional treatment

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methods. Adsorption technique is proved to be an effective process for the removal of color from dye wastewaters, because of its efficiency, flexibility, and economic feasibility.

Activated carbon is the most commonly used adsorbent for the removal of various pollutants from wastewaters. Therefore, finding alternative low-cost materials that have comparable adsorption capacity to activated carbon is highly desired. Among these alternative adsorbents, it can be cited: yellow passion fruit waste [3], fallen phoenix tree's leaves [4], wheat shells [5], olive pomace [6], ground hazelnut shells [7]. The purpose of this paper is to assess the ability of milk thistle seed (MTS) to adsorb MB dye from aqueous solutions with and without the assistance of ultrasound.

Due to the many practical applications of adsorption for removal different types of chemical pollutants and obtained outstanding results in terms of cost—effectiveness of this method, is attempted to improve their performance by combining they with various other techniques (stirring, ultrasound, etc.).

The recent increase in the applications of ultrasound for benign environmental remediation has conducted many researchers to investigate the effects of ultrasound on adsorption and desorption processes [8–17]. The process is based on the phenomenon of acoustic cavitation, involving the formation, growth, and sudden collapse of micro-bubbles in an irradiated liquid. Ultrasound causes the formation of cavitation bubbles leading to high localized temperatures and pressures. On the microscale, high bubble temperatures up to 5,000 K and pressures up to 1,000 atm have been estimated [18–21]. The most pertinent effects of ultrasound on liquid–solid systems are mechanical and are attributed to symmetric and asymmetric cavitation. In addition, shock waves are produced which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as micro-streaming [21]. Asymmetric collapse leads to the formation of micro-jets of solvent that impinge on the solid surface resulting in pitting and erosion. Acoustic streaming is the movement of the liquid induced by the sonic wave, which can be considered to be the conversion of sound to the kinetic energy, and is not a cavitation effect. These phenomena increase the rate of mass transfer near the surface as well as possibly thinning the film [21].

The main objective of this paper is to investigate the adsorption of MB dye from aqueous solution by an adsorbent based on agricultural waste MTS using an adsorption classical process and another resulted by combining adsorption with stirring and ultrasound. It will study the adsorption equilibrium and kinetics for both process in order to find an appropriate combination of ultrasonic irradiation and stirring that could provide maximum efficiency concerning the removal of MB dye from liquid phase.

2. Materials and methods

2.1. Adsorbate

The cationic dye, MB ($C_{16}H_{18}N_3SCl$, see Fig. 1) was obtained from Sigma Chemical Co., USA, with analytical grade that was used without further purification. Required amount of dye was dissolved in double distilled water to prepare 1,000 mg L^{-1} stock solution which was later diluted to working concentrations. In order to adjust the pH solutions, 0.10 mol L^{-1} sodium hydroxide or hydrochloric acid solutions were used, and the measurements were made by using a pH/meter NAHITA 903 provided with combined glass electrode. Distilled water was used for preparing all solutions.

2.2. Adsorbent preparation

Silybum marianum commonly known as milk thistle is an annual or biennial herb, with stem (20–150 cm high), leaves (25–50 cm long and 12–25 cm wide) and fruit (15–20 mm long), and belongs to the family Asteraceae. It is indigenous to North America, Asia, Southern Europe, Russian Federation, naturalized to South and North, America, Australia, China, Central Europe and found wild in NWFP and the Punjab areas of Pakistan. [22]. Also milk thistle is a hardy and often invasive plant indigenous to the Mediterranean region.

White milk thistle used in the present study was collected from the region of Batna, Algeria. The collected MTS were washed with distilled water several times to remove dirt particles and water soluble materials. Then it was oven dried at 50°C for 3 days. The dried seeds were ground and sieved to obtain a particle size with range of 0.5 ± 1 mm. The obtained material was washed repeatedly with distilled water until the wash water contained no color. Finally, the obtained material was dried in an air circulating oven at 50°C for 3 days and stored in a desiccator until use.

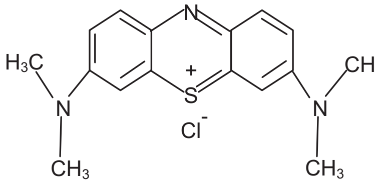

Fig. 1. Chemical structure of MB.

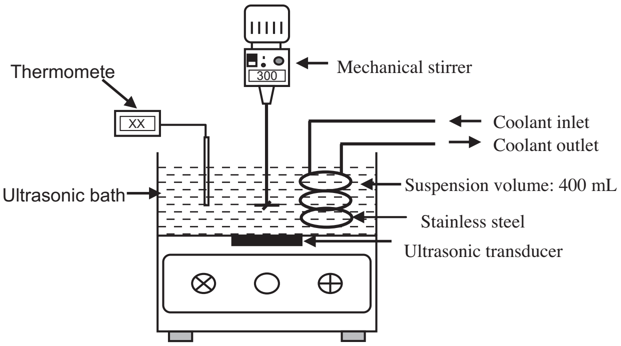

Fig. 2. Experimental installation.

2.3. Experimental installation

The adsorption experiments were carried out in an experimental installation showed in Fig. 2. This consists of an ultrasound bath operating at a frequency of 40 kHz and two ultrasonic powers of 30 and 60 W was used for adsorption experiments under sonication. For each experiment, two thirds of the bath was filled with suspension (the medium for ultrasound propagation) at 25 ± 1 °C. The temperature of the suspension was monitored using a thermocouple immersed in the medium. The temperature inside the ultrasonic bath was kept constant by circulating cooling water within a stainless steel serpentine immersed in the irradiated suspension. Acoustic power dissipated in the medium was measured using standard calorimetric method [23]. For all the experiments, the MB dye solution volume treated was 400 mL.

2.4. Working methodology

Batch adsorption experiments were planned on the basis of variation in three parameters: (i) adsorbent dosage, (ii) ultrasonic power and (iii) initial concentration of the pollutant. The results of the experiments were compared with the adsorption in conventional conditions to assess the enhancement effect of ultrasound.

For dye removal kinetic experiments, previously established dose of MTS was contacted with 400 mL MB dye solutions with initial dye concentration range of 50–200 mg L^{-1}. The mixture was stirred with speed of 300 rpm (conventional method) or simultaneously stirred (300 rpm) and sonicated. At predetermined intervals of time, samples were taken every 10 min in the first hour of the experiments and then every 30 min until equilibrium samples of supernatant were taken and the dye concentrations were measured by a double beam UV/Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 664 nm. Each experiment was duplicated under identical conditions. Each experimental run continued until no significant change in the dye concentration was measured. Spectrophotometrical determinations were made using calibration curve method that involves graphical plotting the dependence between absorbance and concentration. The amount of retained dye at equilibrium, q_e (mg g^{-1}), was calculated by:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \tag{1}$$

where C_0 and C_e (mg L^{-1}) are the concentrations of MB dye at initial and equilibrium time, respectively, V (L) is the volume of the dye solution and W (g) is the mass of adsorbent used.

Equilibrium isotherms were determined by contacting a fixed mass of adsorbent (0.2 g) with 400 mL of MB dye solutions at 25 ± 1 °C with initial dye concentration range of 50–200 mg L^{-1}. The mixture was then agitated at a constant speed of 300 rpm. For the isotherm determined by associating stirring and sonication, the mixture was simultaneously agitated and sonicated and the temperature was reached the 25 ± 1 °C. After equilibrium, the solutions were analyzed for the remaining MB dye concentration by using a UV–Vis spectrophotometer.

2.5. Determination of active sites

Acidic and basic sites on MTS were determined by the acid–base titration method proposed by Boehm [24]. The total acid sites matching the carboxylic, phenolic, and lactonic sites [24] were neutralized using a 0.1 N NaOH solution while the basic sites were neutralized with a 0.1 N HCl solution. The carboxylic and lactonic sites were titrated with a 0.1 N Na_2CO_3 solution and the carboxylic sites were determined with a 0.1 N $NaHCO_3$ solution, and the phenolic sites were estimated by difference [25].

The acidic and basic sites were determined by adding 50 mL of 0.1 N titrating solution and 1 g of MTS to a 50 mL volumetric flask. The flask was slowly agitated, partially immersed in a constant temperature water bath set at 25 °C, and it was left there for 5 days. Afterward, a sample of 10 mL was titrated with a 0.1 N HCl or NaOH solution. The titration was carried out by triplicate using a potentiometer, Orion, model EA940.

3. Results and discussion

3.1. Surface properties of MTS

The concentrations of total acid and basic sites are displayed in Table 1. The concentration of total acid

Table 1
Concentration of active sites on MTS surface

Acidic sites	
Total (meq g^{-1})	2.15
Phenolic (meq g^{-1})	1.75
Carboxylic (meq g^{-1})	0.05
Lactonic (meq g^{-1})	0.30
Basic sites (meq g^{-1})	0.30

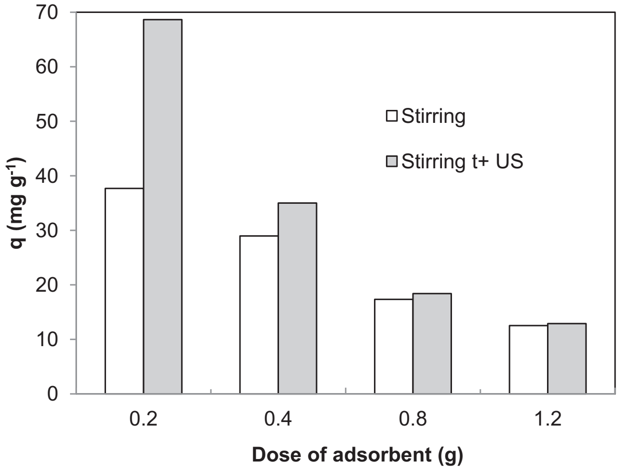

Fig. 3. Effect of adsorbent dosage on MB adsorption by MTS in the absence and presence of ultrasound (conditions: 400 mL of solution, initial MB dye concentration 50 mg L^{-1}, adsorbent amount 0.2–1.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1℃).

sites is larger than that of the basic sites; hence, the surface of MTS is acidic. The capacity of adsorbent for adsorbing MB dye is essentially due to the presence of the acid sites since the dye cations in aqueous solutions can be adsorbed on these sites.

3.2. Effect of adsorbent dose

Before conducting adsorption experiments, the effects of ultrasound on the degradation of MB dye were examined. In our conditions (40 kHz, 30 or 60 W, and MB dye concentrations range of 50–200 mg L^{-1}), the obtained results (data not shown) demonstrate that MB dye degradation was not noticeable until a sonication time of 10 h.

To investigate the effect of adsorbent dose on MB dye adsorption, experiments were conducted at initial dye concentration of 50 mg L^{-1}. When it was used ultrasound, the acoustic power used was 60 W. The effect of adsorbent dose on MB dye adsorption in the two cases was shown in Fig. 3. In both cases, it was observed that the amount of MB dye adsorbed per unit mass of adsorbent decreased from 37.68 to 12.52 mg g^{-1} in the conventional method and from 68.64 to 12.90 mg g^{-1} in the combined method (ultrasound + stirring) with increase in adsorbent dose from 0.2 to 1.2 g, respectively (Fig. 3).

For all adsorbent dosages, it was observed that adsorption was more effective in the presence than in the absence of ultrasound. For the higher adsorbent dosage, the increase of adsorption in the presence of ultrasound is low that is due to the high availability of adsorption sites. For the lower adsorbent amount, the improvement is significant. Recently, similar observation was reported [11]. This behavior could be related to the physical effects of ultrasound and cavitation, which give rise to strong convection in the medium also when the bubble is collapsing near the solid surface, symmetric cavitation is hindered and collapse occurs asymmetrically. The asymmetric collapse of bubbles in a heterogeneous system produces high-speed microjets. Additionally, symmetric and asymmetric collapses generate shockwaves, which cause extremely turbulent flow at the liquid–solid interface, increasing the rate of mass transfer near the solid surface. Furthermore, sonication could produce not only high-speed microjets but also high-pressure shock waves and acoustic vortex microstreaming [11,21,26].

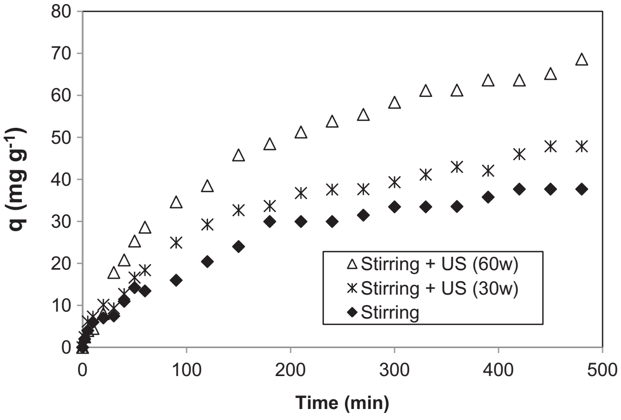

Fig. 4. Effect of ultrasonic power on the adsorption of MB dye by MTS (conditions: 400 mL of dye solution, initial MB dye concentration 50 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 30 or 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1℃).

3.3. Effect of ultrasonic power

The effect of acoustic power of ultrasonic irradiation on the adsorption of MB dye by MTS is shown in Fig. 4. It was observed from Fig. 4 that the adsorption efficiency increased with increasing acoustic power from 30 to 60 W. The adsorbed amount increased from 37.68 mg g^{-1} for the conventional method to 47.88 mg g^{-1} for the combined method (ultrasound (30 W) + stirring) and to 68.64 mg g^{-1} when the mixture was simultaneously agitated and sonicated at 60 W. This could be explained by the fact that at higher power, the cavitation is more intense and leads to enhancement of mass transfer in the system. This behavior can lead to higher effects on the adsorption process [8,9].

3.4. Effect of initial dye concentration

Figs. 5 and 6 showed the adsorption of MB dye in the absence of ultrasound and in the combined process (sonication and mechanical stirring) for various initial dye concentrations and a adsorbent amount of 0.2 g as a function of contact time. It can be seen that the adsorption at different concentrations is rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium is reached. It was observed that the amount of MB dye adsorbed at equilibrium increased with the increase in initial dye concentration. The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. Hence, a higher initial concentration of MB dye will enhance the adsorption process. When the initial MB dye concentration increased from 50 to 200 mg L^{-1}, the loading capacity of MTS increased from 37.68 to 42.82 mg g^{-1} for the conventional method and from 68.64 to 150 mg g^{-1} for the combined method, respectively.

It was clearly shown in Figs. 5 and 6 that ultrasound improves and enhances the adsorption of MB dye by MTS especially for the most concentrated solution. The enhancement of adsorption by associating ultrasound and stirring was 79.5 and 250% for initial dye concentration of 50 and 200 mg L^{-1}, respectively. Therefore, the effect of ultrasound irradiation was significantly increased with the increase of adsorbate initial concentration. This improvement may be explained by the intensification of mass transfer phenomena through acoustic vortex microstreaming, shockwaves, microjets, and thermal effects of ultrasound.

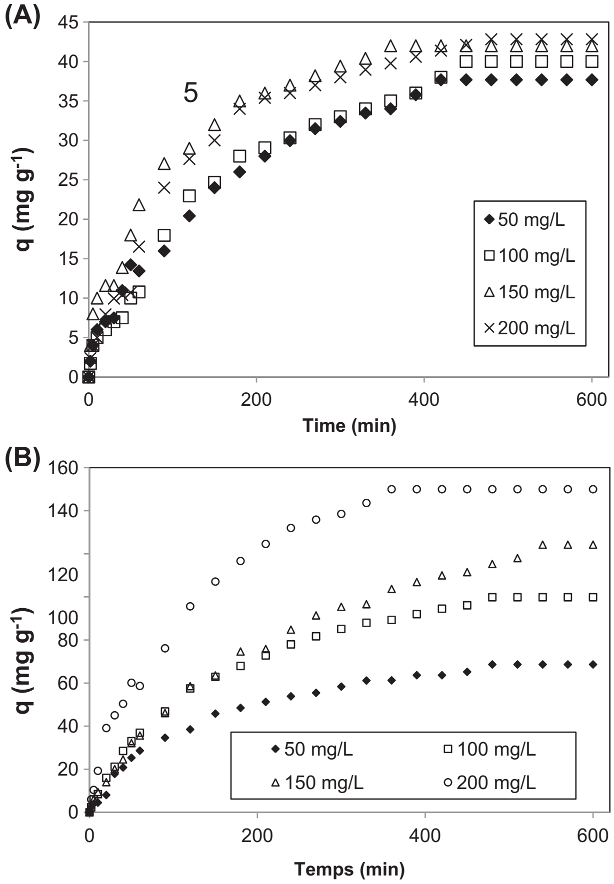

Fig. 5. Effect of initial dye concentration on the adsorption of MB dye by MTS: (A) conventional method and (B) combined method (conditions: 400 mL of dye solution, initial dye concentration 50–200 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1°C).

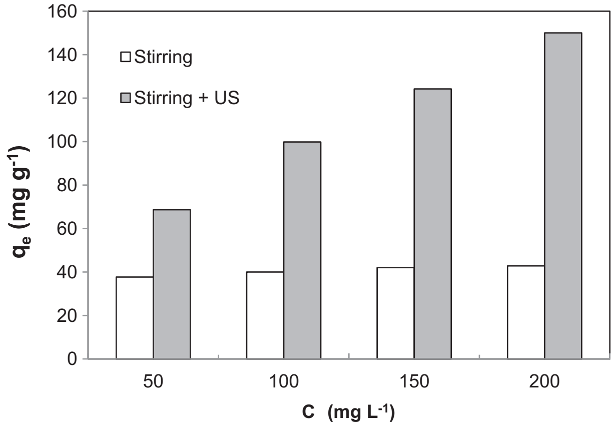

Fig. 6. Effect of initial dye concentration on the amount of MB dye adsorbed at equilibrium (conditions: 400 mL of dye solution, initial dye concentration 50–200 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1°C).

3.5. Isotherm analysis

Equilibrium data in terms of adsorption isotherm is a basic requirement for the design of adsorption systems. The equilibrium removal of dyes was mathematically expressed in terms of Langmuir, Freundlich and Temkin adsorption isotherms models.

The Langmuir [27] isotherm models is based on the assumption that maximum adsorption corresponds to saturated monolayer of the adsorbate molecule on the adsorbent surface. The linearized form of the Langmuir isotherm is described by the Eq. (2)

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m} \tag{2}$$

The constant b (L/mg) is related to the energy of adsorption, C_e (mg/L) is the equilibrium concentration of the dye in solution, q_e (mg/g) is the amount of adsorbed dye on the adsorbent surface and q_m represents the maximum binding at the complete saturation of adsorbent binding sites. q_m and b values can be obtained from slope and intercept of the linear plot of C_e/q_e vs. C_e (Fig. 7), respectively and the values are given in Table 2. The determination coefficient values suggest that the Langmuir isotherm provides a good fit to the isotherm data for the two studied methods ($r^2 \geqslant 0.969$).

The Freundlich [28] isotherm model suggests that adsorption energy exponentially decreases on completion of the adsorptional sites of adsorbent. This isotherm is an empirical model employed to describe heterogeneous systems. The linearized form of the Freundlich isotherm model is described by the following equation:

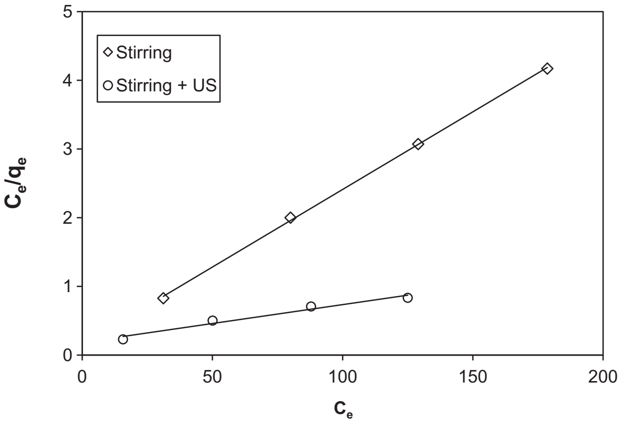

Fig. 7. Langmuir adsorption isotherm for MB dye by MTS (conditions: 400 mL of dye solution, initial dye concentration 50–200 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1℃).

Table 2
Isotherm parameters for the adsorption of MB dye by MTS at 25℃

	Stirring	Stirring + ultrasound
Langmuir		
b (L mg^{-1})	0.1491	0.0299
q_m (mg g^{-1})	44.25	181.49
r^2	0.9995	0.9686
APE (%)	1.51	9.23
Freundlich		
n	13.39	2.72
KF (mg$^{1-(1/n)}$L$^{1/n}$ g^{-1})	29.06	24.49
r^2	0.99005	0.99018
APE (%)	0.58	2.75
Temkin		
a_t (L mg^{-1})	8839.86	0.36
b_t (J mol^{-1})	826.58	66.39
r^2	0.98755	0.95401
APE (%)	0.47	5.77

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where, K_F and n are the physical constants of the Freundlich isotherm. The slope and intercept of the linear plot of ln q_e vs. ln C_e (Fig. 8) give the values of n and K_F.

The magnitude of the exponent n gives an indication on the favorability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [29]. The Freundlich constants are given in Table 2. The result shows that the values of n are greater than 2 indicating that the dye is favorably adsorbed by MTS. The results of the present investigation indicate that besides the Langmuir isotherm, Freundlich isotherm is also suitable for describing the adsorption of MB dye on MTS ($r^2 \geqslant 0.99$).

The Temkin [30] isotherm model assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by the following equation:

$$q_e = \frac{RT}{b_t} \ln a_t + \frac{RT}{b_t} \ln C_e \tag{4}$$

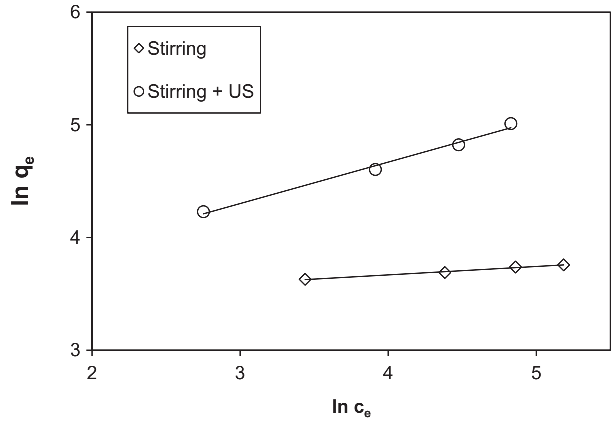

Fig. 8. Freundlich adsorption isotherm for MB dye by MTS (conditions: 400 mL of dye solution, initial dye concentration 50–200 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1 °C).

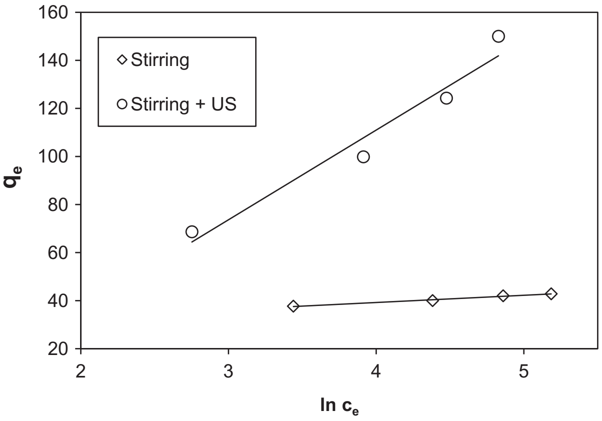

Fig. 9. Temkin adsorption isotherm for MB dye by MTS (conditions: 400 mL of dye solution, initial dye concentration 50–200 mg L^{-1}, adsorbent amount 0.2 g, ultrasonic power 60 W, stirring speed 300 rpm, natural pH (5.3), temperature 25 ± 1 °C).

where b_t is the Temkin constant related to the heat of adsorption (J mol^{-1}), a_t is the Temkin isotherm constant (L mg^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). The a_t and b_t values could be calculated from the linear plot of q_e against ln C_e (Fig. 9) and are given in Table 2. The determination coefficient values suggest that the Temkin isotherm provides an acceptable fit to the isotherm data for the two studied methods ($r^2 \geqslant 0.954$).

In order to compare the validity of isotherm equations more definitely an average percentage errors (APE) is calculated as follows:

$$\mathrm{APE}(\%) = \frac{\sum_{1}^{N}\left|\frac{(qe)\exp-(qe)cal}{(qe)\exp}\right|}{N} \times 100 \tag{5}$$

where the subscripts "exp" and "cal" show the experimental and calculated values and N is the number of experimental data. The determination coefficients (r^2) showed the fit between experimental data and isotherm equations, while the APE calculated according to Eq. (5) indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves. The Freundlich and Langmuir models gave the highest determination coefficient values which were greater than 0.969 for the two studied methods and the lowest APE, showing that the adsorption isotherms of MB dye by MTS were best described by Temkin and Freundlich models especially for the conventional method.

The values APE and determination coefficients given in Table 2 attest that the adsorption isotherm data could be well simulated by Freundlich isotherm model, and then Temkin and Langmuir isotherm models. The maximum adsorption capacities calculated were 44.25 and 181.49 mg g^{-1} for the conventional method and the combined method, respectively.

Table 3 lists a comparison of adsorption capacity of the MTS with those obtained in the literature for the adsorption of MB. The calculated adsorption capacities exhibit a good capacity for dye adsorption from aqueous solutions. This result reveals that the MTS is effective adsorbent for MB dye from wastewater when it was using a combined method. It should be noted that the values and comparisons reported for MB dye

Table 3
Comparison of adsorption capacity of the MTS with that of various adsorbents

Sorbent	q_m (mg/g)	Reference
Yellow passion fruit waste	44.70	[3]
Fallen phoenix tree's leaves	83.8 ± 7.6	[4]
Wheat shells	16.56	[5]
Olive pomace	42.3	[6]
Charcoal	62.7	[6]
Ground hazelnut shells	76.9	[7]
Walnut sawdust	59.17	[7]
Cherry sawdust	39.84	[7]
Oak sawdust	29.94	[7]
Pitch-pine sawdust	27.78	[7]
Posidonia oceanica (L.) fibres	5.56	[31]
Glass wool	2.24	[32]
MTS (conventional method)	44.25	This work
MTS (ultrasound assisted method)	181.49	

removal capacity have only a relative meaning because of different testing conditions and methods.

4. Conclusion

This study shows that MTS can be used as an adsorbent for the removal of MB dye from aqueous solutions. The amount of MB dye adsorbed was influenced by initial dye concentration, adsorbent dose and ultrasonic power. The amount of MB dye adsorbed in the presence of ultrasound and stirring was improved with the increase of adsorbate initial concentration and ultrasonic power, and with the decrease of adsorbent dosage.

Adsorption data could be well simulated by Freundlich isotherm model, and then Temkin and Langmuir models. The maximum adsorption capacities calculated by using the Langmuir isotherm were 44.25 and 181.49 $\mathrm{mg\,g^{-1}}$ for the conventional method and the combined method, respectively. The connection of ultrasound and stirring to the process was shown to be of interest for the treatment of wastewaters contaminated with cationic dye such as MB dye.

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