

Modification of Waste Wool Fiber as Low Cost Adsorbent for The Removal of Methylene Blue from Aqueous Solution

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REMOVAL of methylene blue (MB) from water using adsorbent developed from waste wool fiber has been investigated by batch adsorption experiments in the present work. Wool fiber waste (WF) was collected from a local Spinning and Weaving Company, cleaned and further treated with citric acid to increase its adsorption capacity toward basic dyes. Raw and treated WF were ball milled to produce wool powder (WP) and modified wool powder (MWP), respectively. The carboxyl content was increased steadily as the citric acid solution concentration increased. The introduction of the carboxyl groups also has been proved by streaming potential measurements. The effect of contact time, wool dose and dye solution pH on the adsorption process were studied too. The adsorption isotherm was examined using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) models. The adsorption equilibrium was attained within 20 minutes with a maximum removal percentage of 70 and 78 for WP and MWP, respectively. The wool dose affects the adsorption process significantly, especially for MWP which removes a higher percentage of MB (86 %) compared to WP (75 %). Both Freundlich and D-R were well fitting the adsorption equilibrium data with $R^2 > 0.9$. The values of Freundlich exponent factor (n) and D-R adsorption energy (E) reveal the chemisorption nature of the MB adsorption on both WP and MWP. This work demonstrated that, chemical and physical modifications of the waste wool fiber with citric acid has enhanced the adsorption of MB.

Keywords : Dye removal , Wool fiber waste , Isotherm modeling , Adsorption, Wastewater treatment.

Introduction

Water pollution by dyes is a worldwide problem particularly in textiles, leather, paper, plastics, rubber, cosmetics, pharmaceutical and food industries where large quantities of dye effluents are discharged into the surface water bodies without appropriate treatment [1,2]. Discharge of these dyes presents a major environmental problem for developing countries because of their toxic and carcinogenic effects on living beings, consequently, dyes become a momentous source of water pollution even at trace level [3, 4].

Methyleneblue (MB), 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride, is one of the widely used cationic azo dyes in the industry[5]. The presence of MB in the aquatic environment deteriorates the water quality and causes several harmful effects on human and aquatic life. For example, it reduces the photo synthesis process

and hampers the ability of aquatic organisms to localize food by interfering the penetration of sunlight and increasing the turbidity in water bodies, correspondingly. Also, it biodegrades slowly thus lasts for a long time in the water bodies and contaminates the food chain. Therefore, the removal of MB from the aquatic environment is of significant concern [1-3].

Several techniques such as adsorption, photocatalytic degradation, biodegradation, and electro coagulation have been reported in the literature [6-10] for the removal of MB from the aqueous medium, however, the high efficiency, flexibility, ease of operation, simplicity, low cost, and insensitivity to toxic pollutants features make the adsorption technique the most attractive and widely used [1-3, 11]. Nowadays, studies are focused on utilizing agricultural and industrial wastes as adsorbents for dye removal due to their

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abundance, low cost, low commercial value, and biodegradability [1, 2, 12-15].

Waste wool fibers are amply available in Egypt. Utilizing this waste as adsorbent material could cut the cost of adsorption process and provide a solution for waste management [16-22]. The presence of functional groups (such as NH₂, CONH₂, COOH, and OH) in the wool [18, 20] makes it a promising sorbent. These groups render wool high binding capacity toward metal ions [20, 23, 24] and dyes [25, 26]. In addition, grinding wool into fine powder enhances the wool binding capacity owing to an enormous increase in the specific surface area, meanwhile, keeping the original features of the wool unchanged [18, 20, 27]. Further enhancement in the wool binding capacity might be attained by chemical modification. It worth noting that the oxidation of wool using a mixture of hydrogen peroxide and Tetraacetythylenediamine (TAED) improved the wool exchange-ability toward copper and zinc [20].

This study aims at utilizing the abundant waste wool fiber as a low-cost sorbent for dyes removal. The waste wool fiber was treated physically by ball milling and chemically by citric acid to enhance its adsorption capacity. The adsorption performance of the physically and chemically treated waste wool fiber was assessed and compared under different conditions such as aqueous medium pH, sorbent dose, contact time, and initial dye concentration. Finally, the adsorption equilibrium data was modeled using Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) equations.

Materials And Methods

Chemicals

Wool fiber waste (WF) was supplied by El-Shemy Co for Spinning and Weaving, 10th of Ramadan, Egypt. The characters of these wool fibers are summarized as follows: mean fiber diameter 19.9 μm, fiber strength 10.2 cN/tex, and alkali solubility 15.7%. The fibers were subjected to scouring process using 1 g/L sodium carbonate and 1 g/L non-ionic detergent at 60°C for 10 min to remove the oily matters added during the carding and combing processes. Wool fibers were then thoroughly rinsed with cold water, squeezed, and finally, air dried at ambient temperature.

Citric acid mono hydrate (C₆H₈O₇·H₂O) from

Merck (Germany) was used to modify the WF. Sodium hypophosphite (NaH₂PO₂·H₂O) from Ridean de hean (Germany) was used as a catalyst. Analytical grade chemicals were supplied by Merck (Darmstadt, Germany) and used as received.

Wool fiber modification

The wool modification was carried out by firstly treating the wool fibers with 0.01-0.1 molar citric acid solution with about 4 % sodium hypophosphate as a catalyst bearing numbers of carboxyl groups at a liquid ratio of 1:50, at 75°C for 90 min. Wool fibers were then removed from the treatment solution, thoroughly rinsed and allowed to dry at ambient conditions, further drying was carried out by heating in an oven at 105 °C to attain constant weights. The dry weight of wool samples was determined before and after treatment [28].

Powder preparation

Wool fibers (WF), as well as citric acid modified wool fibers (MWF), were both milled separately using the ball milling technique (Retsch PM 100, Germany), equipped with zirconium balls, to produce wool powder (WP) and citric acid modified wool powder (MWP). The total milling time was adjusted for 8 hours after each 10 min takes a rest for 5 min and start in a reverse direction [20].

Dye solution

Methylene blue (MB) was used as the adsorbate in this study. MB is a cationic thiazine dye with the molecular formula of C₁₆H₁₈ClN₃S, molar mass of 373.90 g/mol and a maximum absorbance peak in the visible region at a wavelength of 664 nm. The chemical structure of MB is shown in Fig. 1.

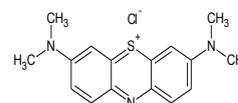


Figure 1. Chemical structure of MB.

A fresh working solution of MB was prepared for each experiment by dilution of 1g/L stock solution to give the desired initial concentration. Deionized water was used to prepare all solutions. The initial pH of the working solutions without adjustment was 6.5.

Wool characterization

Surface morphology analysis

The surface morphology of wool fibers and its powders were studied by using HITASHI S-3000 (Hitachi, Japan) microscope, at 15-kV acceleration voltage. The powder surface is coated with a thin layer of gold by Edwards S150B Gold Sputter Coater in order to perform the SEM photos.

Carboxyl content of wool fiber

Initially pure wool as well as modified wool samples were treated with 0.001 N HCl solution for 48hr, then washed with distilled water several times until constant pH value and samples were then dried in air. Dry wool (5 g) was wetted in 100 mL solution of NaOH (0.3 N) saturated with sodium chloride at 25 °C for one hour. Wool samples were removed and 10 mL of the alkaline solution was titrated against standard HCl, and the alkali combining capacity is calculated as follows in Eq. (1) [28]:

$$\text{COOH content (meq./100g wool)} = \left(\frac{V_b - V_s}{W_t} \right) 100 \quad (1)$$

where : V_b is the volume of HCl corresponding to NaOH.

V_s is the volume of HCl corresponding to samples.

W_t is the weight of wool sample.

Streaming potential measurements

Electrokinetic measurements were carried out to determine the electrokinetic potential (ζ) of the wool fiber surface as a function of the pH values of the electrolyte solution using the streaming potential method. The streaming potential was determined using EKA electrokinetic analyzer (Anton Paar GmbH, Graz, Austria) using the cylindrical cell, which was developed for the measurement of fibrous samples. The measuring cell consists of a glass cylinder with inlet and outlet tubes for the electrolyte solution. The fiber sample is mounted between a pair of perforated Ag/AgCl disc electrodes. The electrodes are mounted onto movable pistons, which allow a variation of the distance between these electrodes. The pH values were adjusted with 0.1 mol/L HCl or 0.1 mol/L KOH. To prevent a significant change in the ionic strength by adding HCl and KOH, all measurements were carried out in 10-3 mol/L KCl, which is known as an inert electrolyte. The zeta-potential values were calculated from the measured streaming potentials by the use of the Smoluchowski equation [29]. The streaming potential experiments were carried out with the

Electro Kinetic Analyzer (EKA) (Anton Paar GmbH, Graz, Austria).

Adsorption experiments

Batch adsorption experiments were carried out at $25 \pm 0.1^\circ\text{C}$ by adding the wool samples to a series of 100 mL of 20 mg/L MB solution (pH 6.5) in a 250 mL stopper conical flasks. After shaking at 120 rpm, samples were withdrawn, filtered, and the MB concentration in the filtrate was measured using a UV-Vis spectrophotometer (Shimadzu UV-2600) at wavelength 664 nm. The removal percentage (R %) was calculated by Eq. (2).

$$R \% = \left(\frac{C_o - C_e}{C_o} \right) 100 \quad (2)$$

where C_o and C_e are the initial and equilibrium concentration of MB in the solution (mg/L).

For each series of measurements, duplicate samples, MB standard, and a procedural blank were analyzed. Also, the spectrophotometer was calibrated regularly and calibration was verified before each sample set. The R % of MB in the procedural blank was insignificant. Mean values of the duplicate samples were used in calculations.

Contact time effect.

0.3 g of the wool samples were added to 100 mL MB solutions and the flasks were shaken for 100 min. Samples were withdrawn at a pre-set time intervals, and the procedure continued as described above.

Wool amount effect.

Different weights of the wool samples (1 to 10 g/L) were mixed with MB solutions. After shaking for 1 h the samples were filtered, and MB concentration in the filtrate was determined.

pH effect.

0.9 g of wool samples were shaken for 1 h with 100 mL MB solutions per-adjusted to pH 3 to 7 then the above-mentioned procedure was continued. The solution pH was adjusted by 0.1 M HCl or 0.1 M NaOH solutions and was measured by a digital pH-meter (GOnDO PL-700PV).

Isotherms study.

In order to optimize the design of adsorption system, it is important to analyze the adsorption equilibrium data. For this purpose, initial MB concentrations ranging between 10 to 100 mg/L

were used to study the adsorption isotherms. The solution pH was 6.5 and the wool dose was 9 g/L. The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models were applied to describe the mechanism of MB adsorption on the wool sample and describe the surface properties and affinity of the wool samples.

The Langmuir model

The Langmuir model [30] is based on the assumption of the uniform adsorbent surface with adsorption sites of the equal energy of adsorption, availability, and number of molecules that can be carried. Eq. 3 gives the linear form of Langmuir model.

$$\frac{C_e}{q_e} = \frac{1}{Q K_L} + \frac{1}{Q} C_e \quad (3)$$

where Q (mg/g) is the Langmuir maximum adsorption capacity, K_L (L/mg) is the Langmuir constant related to the equilibrium of adsorption, and q_e (mg/g) is the equilibrium dye concentration per gram of wool which was calculated by Eq. 4;

$$q_e = \frac{(C_o - C_e) V}{W} \quad (4)$$

where W is the weight of wool (g) and V is the volume of MB solution (L).

Conversely, Freundlich model [31] assumes a heterogeneous adsorbent surface with adsorption sites of different energy of adsorption, and availability. The linear form of Freundlich model is shown in Eq. 5.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The Dubinin–Radushkevich model

The Dubinin–Radushkevich model [32] predicts the nature of the adsorption process either physical or chemical. The linear form is given in Eq. 6;

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (6)$$

where q_m is D–R's monolayer capacity (mg/g), β is

constant related to adsorption energy and ε is Polanyi potential, which can be calculated by Eq. 7;

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R is the ideal gas constant (8.314 J/mol K), and T is the absolute temperature (K). The value of β derived from Eq. 5 was used to calculate the adsorption energy (E) according to Eq. 8;

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

Results and Discussion

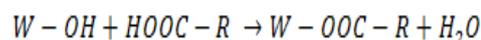
Characterization

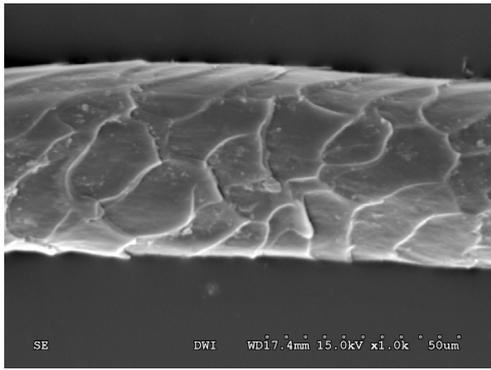
Surface morphology

Figure 2 shows the SEM of wool fiber, modified wool fiber (0.07 molar citric acid solution), wool powder and modified wool powder. Figure 2 (A and B) shows the normal structure of wool fibers as well as it clarifies the existence of the scale structure of wool fibers after citric acid modification step. Figure 2 (C and D), elucidates that both wool powder and modified wool show heterogeneous particle size distribution. It is worth noting that, regarding our previous research [20] the milling process of wool fibers at similar milling conditions leads to an increase in the specific surface area from (0.97 m²/g) to (259 m²/g) for WF and WP, respectively.

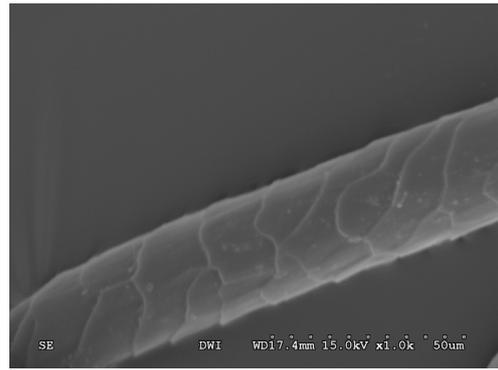
Alkali Combining Capacity

The effect of citric acid solution concentration on the alkali combining capacity (carboxyl content) of the wool fiber was investigated. Figure 3 illustrates the relation between the carboxyl content (meq./100 g wool) of unmodified and modified wool versus citric acid solution concentration. It was observed that the carboxyl content was increased steadily as the citric acid solution concentration increased, till reaching a maximum value of 670.9 meq./100 g wool at citric acid conc. of 0.07 molar. After which no appreciable increase was observed and so the wool sample of carboxyl content of 670.9 meq./100 g wool was milled and used for dye removal study. Proposed reactions between wool fiber and citric acid were illustrated in Eq. 9 and 10;

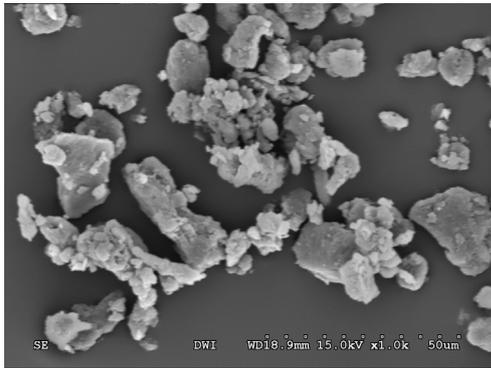




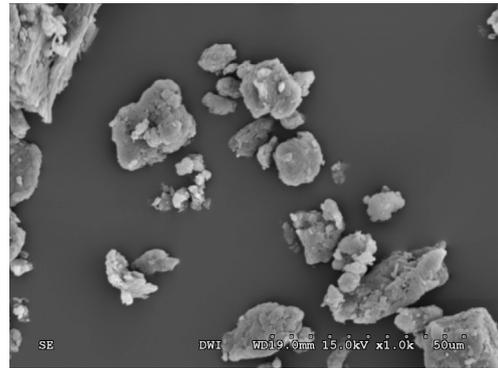
A: Wool Fiber



B: Modified wool fiber



C: Wool powder (WP)



D: Modified Wool powder (MWP)

Fig. 2. SEM of wool fiber, modified wool fiber, wool powder and modified wool powder.

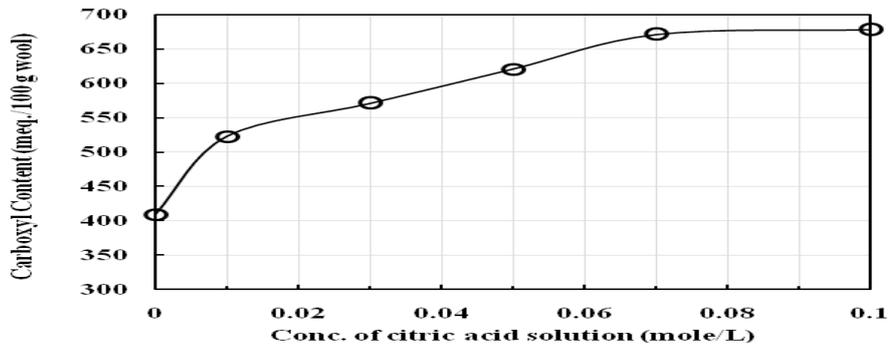
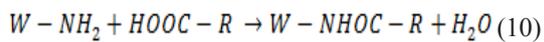


Fig. 3. The relation between conc. of the citric acid solution and the carboxyl content of wool fiber.



where W-OH and W-NH₂ are wool fiber, HOOC-R is citric acid

Streaming potential measurements

The introduction of the Brønsted-acidic

carboxyl groups can be additionally proved by streaming potential measurements that are very sensitive to analyze charge formation processes on solid surfaces. Figure 4 shows the determined zeta-potential values (ζ) for the unmodified and citric acid modified wool fibers as a function

of the pH values of an aqueous KCl with a concentration of 10⁻³ mol/L solution. At pH < 5.2, the zeta-potential of the unmodified wool fiber is positive because of the adsorption of H₃O⁺ ions from the electrolyte solution onto the fiber surface. With increasing the pH value, zeta-potential decreases. At pH = 5.2 there is neither an excess of negative nor positive charges in the shear plane where the numbers of protonated amino groups and deprotonated carboxylic acid groups approximately equal [33]. Therefore, the corresponding zeta-potential is zero. The pH value where zeta-potential equals to zero is called the isoelectric point (IEP = pH| $\zeta=0$). At pH > IEP, (-ev) zeta-potential values are detected, which could be attributed to the preferential adsorption of hydroxide ions from the electrolyte solution.

Influence of treatment wool fibers with citric acid was also investigated by use of streaming potential measurements. Figure 4 shows that in comparison with the unmodified wool fiber surface, IEP shifted to lower pH values. The IEP shift is mainly obtained by the existence of negatively charged carboxylate groups (O=C-O⁻), which are taking part to the overall surface charge [34].

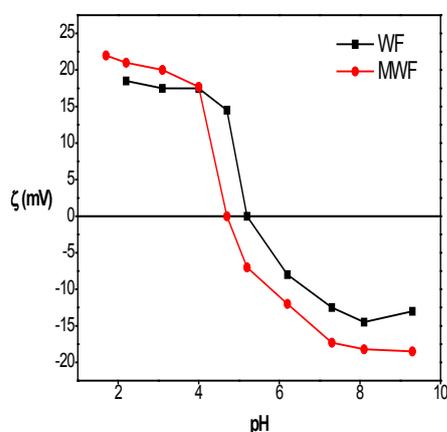


Fig. 4. Zeta potential for unmodified wool fabric (WF) and modified wool fabric (MWF) with citric acid as a function of pH (in 1 mM KCl).

Optimum conditions

Effect of contact time

Figure 5 displays the percentage of MB removed by the studied wool samples against contact time. It is obvious that the dye removal is a fast process that occurs in the beginning of

contact time, up to 15 minutes. But prolonging the contact time over 20 minutes causes slight dye desorption. In addition, it is observed that the wool sample MWP removes 78% of MB in the first 15 minutes which is higher than the percentage removed by WP (70%) at the same period. This observation might be due to the higher carboxyl content of MWP which leads to higher MB removal through electrostatic attraction between the positively charged MB (solution pH > pK_a, MB) and the negatively charged surface of MWP (solution pH > pH_{pzc}).

Effect of dose

Figure 6 shows the removal of MB by different doses of the studied wool samples. It is seen from the figure that the removal percentage increases with increasing the dose of wool samples. This might be owing to the increase of adsorption sites. A significant increase occurs at wool doses from 1 to 5 g/L and from 1 to 3 g/L for MWP and WP, respectively. Further increase in the wool dose to 7 g/L resulted in slight increase in the MB removal percentage, which remains constant thereafter. This might be a consequence of the formation of wool aggregates at high doses. Noteworthy that the effect of dose was more obvious for MWP which removes a higher percentage of MB (86 %) compared to WP (75 %).

Effect of pH

The aqueous medium pH plays an important role in the uptake of the adsorbate due to the variation of the chemical characteristics of both adsorbate and adsorbent with pH. The effect of solution pH on the adsorption of MB on wool samples is shown in Fig. 7. It can be seen that the removal of MB increased with increasing the initial solution pH to 5 then remain almost constant for both WP and MWP. However, when the pH increased to 6.5 an insignificant effect (≤ 5%) on the removal percentage can be observed, decrease for WP and increase for MWP. The low removal percentage observed at pH less than 5 might be due to the existence of H₃O⁺ ions that competes the MB cationic groups for the adsorption sites [35]. When the pH of the solution increases, the surface charge density decreases, therefore, the electrostatic repulsion between the cationic groups in the dye molecule and the wool surface decreases and the removal percentage increases.

Equilibrium studies and isotherm modeling

Langmuir model

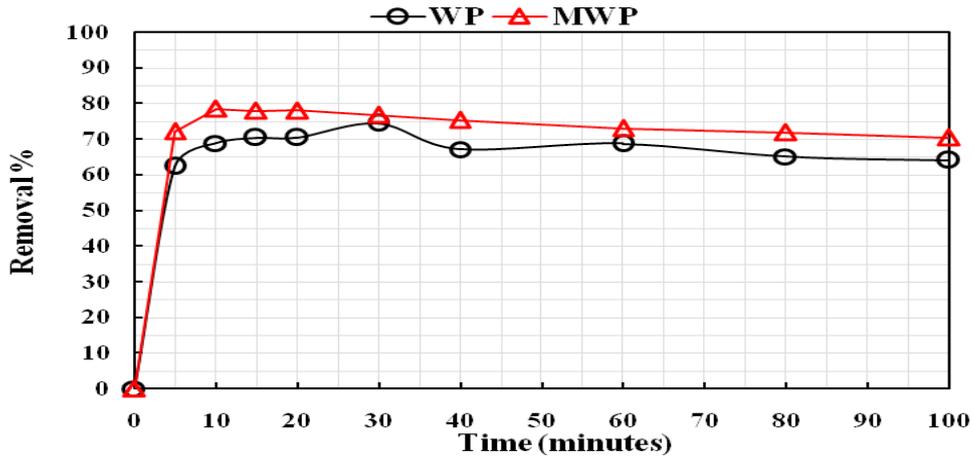


Fig. 5. MB removal percentage as a function of contact time. $C_0 = 20$ mg/L; wool dose = 3 g/L; pH = 6.5.

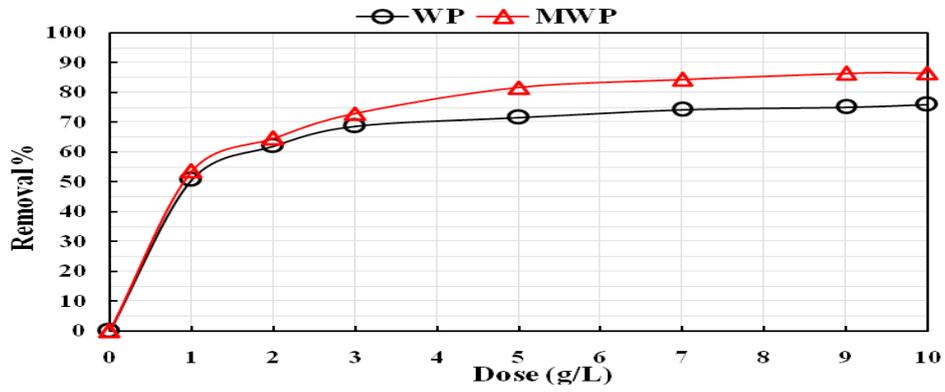


Fig. 6. MB removal percentage as a function of wool dose. $C_0 = 20$ mg/L; contact time = 1 hr; pH = 6.5.

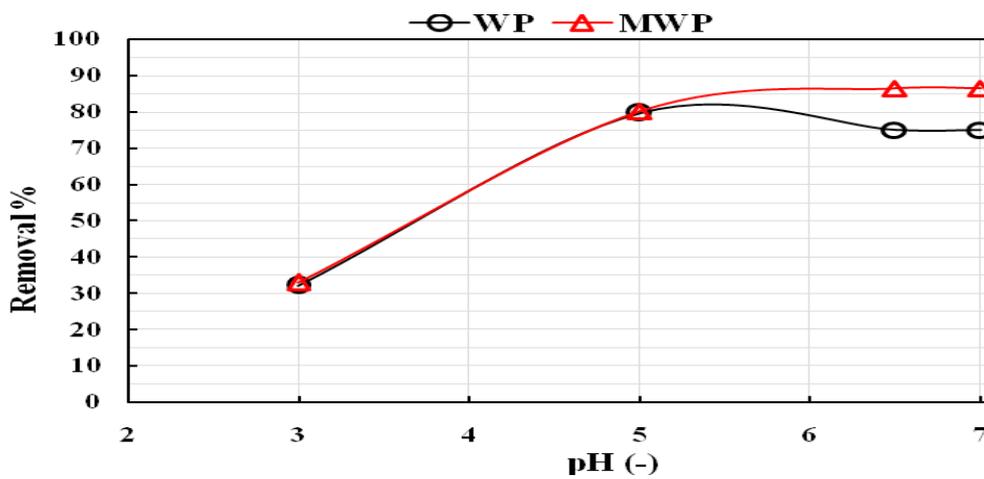


Fig. 7. MB removal percentage as a function of initial solution pH. $C_0 = 20$ mg/L; contact time = 1 hr; wool dose = 7 g/L.

Figure 8 illustrates the plot of C_e/q_e versus C_e for the obtained experimental data of the studied samples. The values of the fitting parameters and correlation coefficient are listed in Table 1. The low R_2 values show that the Langmuir model did not fit the adsorption data. Accordingly, it could not be dependably employed to explain the isotherm data.

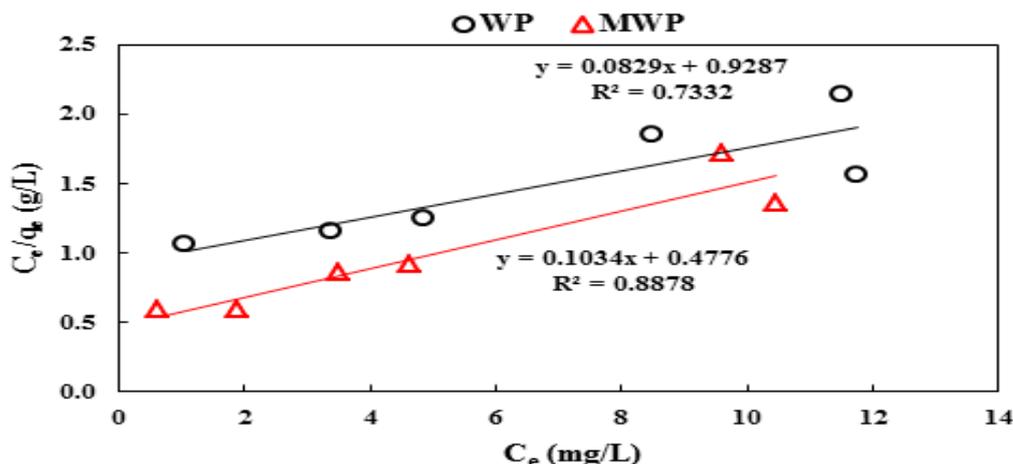


Fig. 8. Langmuir plot for the adsorption of MB on the wool samples, pH 6.5; wool dose 7 g/L; contact time 1 h.

TABLE 1. Calculated isotherms parameters.

Model	Parameter	WP	MWP
Langmuir	R^2	0.73	0.89
	Q	12.06	9.67
	K_L	0.09	0.22
Freundlich	R^2	0.96	0.94
	K_f	1.06	1.70
	n	1.35	1.59
Dubinin-Radushkevich	R^2	0.96	0.95
	E (kJ/mol)	9.69	10.61

a unit equilibrium concentration, WP adsorbs higher quantity of MB than WP. Also, it can be seen that both samples have n values higher than one indicating the favorable adsorption of MB on both samples [36]. In addition, it has to be reported that n values higher than one are indicative of chemisorption [37].

Dubinin-Radushkevich model

The linear plots of the Dubinin-Radushkevich model based on Eq. (5) are presented in Fig. 10 and the calculated isotherm parameters are listed in Table 1. At the adsorption energy (E) ranges from 1 to 8 kJ/mol the adsorption is seemed to be

Freundlich model

A straight line with R_2 values > 0.9 (Table 1) was obtained when $\log q_e$ was plotted versus $\log C_e$ (Fig. 9) suggesting the applicability of the Freundlich model. Consequently, the model parameters, K_f and n, were calculated to extract further interpretation of the isotherm. Table 2 shows that MWP has higher K_f value than WP which mean that, for

a physical adsorption, while when E ranges from 8 to 16 kJ/mol the adsorption is chemical adsorption [38]. Table 1 shows that the E-values for both WP and MWP are in the range of 8–16 kJ/mol, indicating that the type of adsorption is basically chemical. Therefore, both D-R adsorption energy (E) and Freundlich exponent factor (n) suggest that the MB is chemisorbed on the studied wool samples.

Conclusions

It was verified that waste wool powder and citric acid modified waste wool powder might be a potent sorbent material to be applied in the removal of MB from the aqueous medium. The milling process of wool fibers at similar milling conditions leads to an increase in the specific surface area from (0.97 m²/g) to (259 m²/g) for WF and WP, respectively. The carboxyl content was increased steadily as the citric acid solution concentration increased, to reach a maximum value of 670.9 meq./100 g wool. The introduction of the carboxyl groups has been proved by streaming potential measurements. In comparison with the unmodified wool fiber surface, lower IEP shift is mainly obtained by the existence of negatively charged carboxylate groups (O=C-O⁻). Several factors were assessed, including contact

time, wool dose, the solution pH, and initial MB concentration. The optimum conditions were reached at a contact time of 1 hr, wool dose of 7 g/L and at pH 6.5. Adsorption equilibrium data were best fitted by the Freundlich isotherm model, suggesting the formation of multilayer of

MB at the wool surface. Moreover, the interaction between the wool and MB molecules was probably a chemisorption process, as advised by the D-R model.

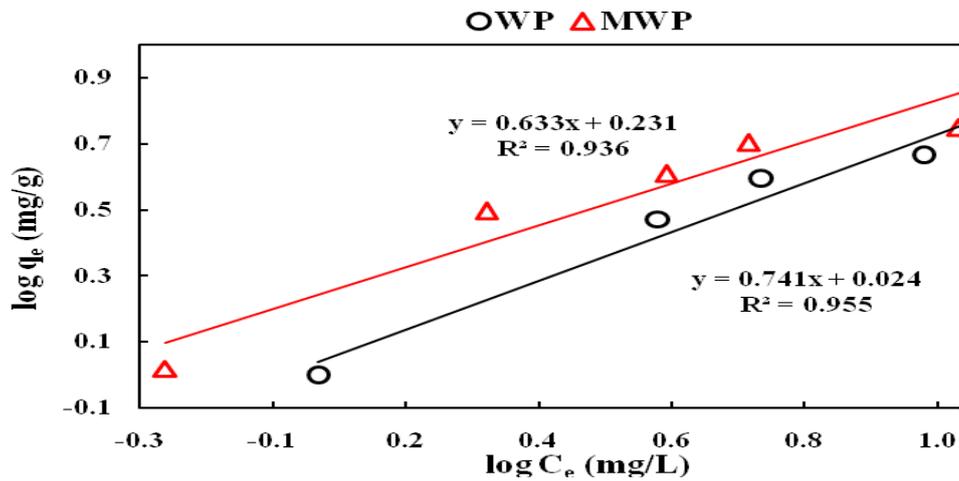


Fig. 9. Freundlich plot for the adsorption of MB on the wool samples. pH 6.5; wool dose 7 g/L; contact time 1 hr.

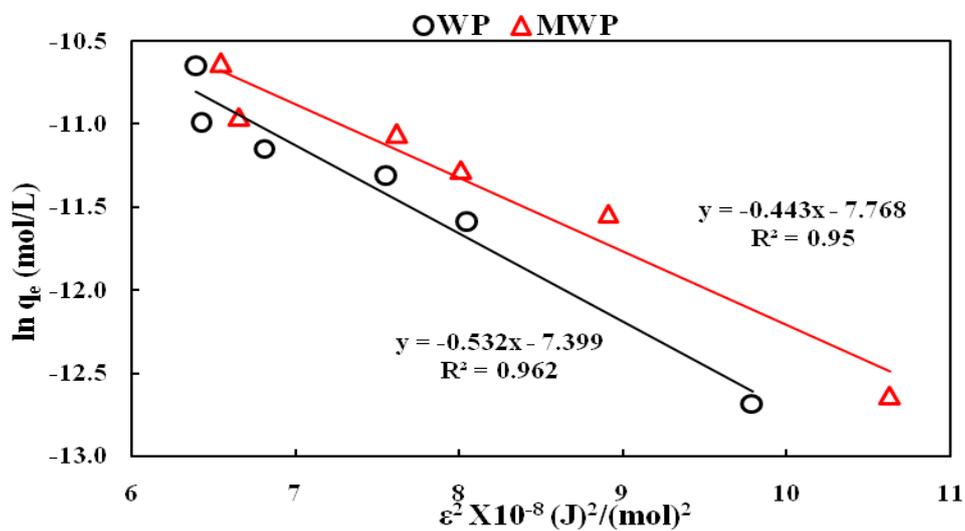


Fig. 10. Dubinin-Radushkevich plot for the adsorption of MB on the wool samples. pH 6.5; wool dose 7 g/L; contact time 1 hr.

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استخدام مخلفات ألياف الصوف المعدلة كمادة مازة منخفضة التكلفة لإزالة صبغة الميثيلين الزرقاء من الأوساط المائية

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تم دراسته إزالة صبغة الميثيلين الزرقاء من المياه باستخدام مواد مازة مطوره من مخلفات ألياف الصوف التي تم جمعها من الشركة المصرية للغزل والنسيج. ولقد تم معالجة مخلفات الياف الصوف بتركيزات من محلول حامض الستريك تم طحنها لزيادة قدرتها على الامتزاز نحو الأصباغ القاعدية. وقد لوحظ زيادة محتوى مجموعة الكربوكسيل على سطح العينات بشكل مطرد مع زيادة تركيز محلول حامض الستريك كما اثبتته قياسات جهد الترشيح الكهربائي. كما تم دراسة تأثير وقت الامتزاز، وكمية المادة المازة، ودرجة حموضة محلول الصبغة على عملية الامتزاز. بالإضافة الى فحص إيثرثرم الامتزاز باستخدام نماذج لانجموير، فريوندلنتش، و دوبينين-رادوشكيفيتش. ووضحت النتائج ان الامتزاز قد وصل الى مرحلة الاتزان في غضون ٢٠ دقيقة مع نسبة إزالة قصوى تراوحت بين ٧٠٪ و ٧٨٪ لمسحوق مخلفات ألياف الصوف قبل وبعد التعديل، على التوالي. كما لوحظ ان كمية الصوف تؤثر بشكل ملحوظ على عملية الامتزاز، خاصة بالنسبة لمسحوق مخلفات ألياف الصوف المعدله والتي تزيل نسبة أعلى (٨٦٪) من صبغة الميثيلين الزرقاء مقارنة بغير المعدله (٧٥٪). واعطى نموذجي فريوندلنتش و دوبينين-رادوشكيفيتش وصفا مناسبيا تماما لنتائج الامتزاز عند الاتزان. ودلت قيم العوامل المستخلصه من فريوندلنتش و دوبينين-رادوشكيفيتش عن الطبيعة الكيميائية لامتزاز صبغة الميثيلين الزرقاء على سطح المواد المازة المستخدمة في هذه الدراسة. خلصت هذه الدراسة الى أن تعديل مخلفات ألياف الصوف كيميائيا بحامض الستريك وفيزيائيا بالطحن قد عزز قدرتها على امتزاز صبغة الميثيلين الزرقاء من المياه. مخلفات الياف الصوف المعدلة تصلح للاستخدام كمادة مازة رخيصة الثمن في معالجة المياه.