



Recycling of Pre-consumer Viscose Waste Fibers for The Removal of Cationic Dye from Aqueous Solution



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RECYCLING of textile waste materials has attracted significant attention for fabrication low-cost dye adsorbent from aqueous solutions. Viscose waste as cellulosic fibers are supposed to give an answer to finding low-cost adsorbent materials. In this research work, viscose fiber wastes (VF) were modified by selective oxidation to improve the ability of absorbing cationic dyes during wastewater treatment. For this purpose, different treatment parameters such as sodium periodate concentration, and time of selective oxidation with sodium chlorite were investigated. Then, unmodified and oxidized viscose fibers (OVF) were ball milled to produce viscose powder (VP) and oxidized viscose powder (OVP), respectively. The morphology of the obtained viscose powders was characterized by scanning electron microscopy. Furthermore, the adsorption of methylene blue (MB) onto viscose cellulose fiber waste and oxidized viscose fibers was studied as a function of contact time (0–80 min), adsorbent dosage (1–9 g/L), MB solution initial pH (3–9) and MB initial concentration (20–80 mg/L). The results showed that MB adsorption onto VP and OVP is a rapid and favorable chemisorption process that can be well described by Langmuir model. The higher adsorption ability of OVP than VP was related to increasing of the carboxylic group. The oxidized viscose fiber can be used as potential adsorbent for wastewater treatment.

Keywords: Viscose fiber, Physical recycling, Powder, Wastewater treatment, Adsorption kinetics, Adsorption isotherms.

Introduction

Lately, environment contamination by manufactured aqueous organic chemicals have attracted wide attention [1]. Dyes are one of the most significant water contaminants due to their diverse and huge usage in textile, leather, paper, plastics, rubber, cosmetics, pharmaceutical and food industries [2, 3]. Dye pollution represents a pressing problem owing to their adverse ecological and human health effects and bulky global production [1, 3-8]. Although, several countries have set strict acts to limit the dye releases, more than 7×10^5 tons of 10,000 types of dyes are still produced yearly, and 10–15% of them are released into the environment [1]. Among these

types of dyes, the highly visible cationic dyes, are recalcitrant, toxic and has adverse effects including skin irritation, allergic dermatitis, mutations, cancer and tissue necrosis [2]. Therefore, efficient removal of dyes from aquatic system has become an urgent challenge for scientists [1, 2, 5, 7, 8].

Numerous treatment techniques, like coagulation, flocculation, precipitation, anaerobic/aerobic biological degradation, ion exchange, solvent extraction, adsorption, advanced oxidation processes, and membrane filtration have been applied to remove dyes from aqueous solutions [1, 7-10]. But, the simplicity, flexibility, high efficiency, cost effectiveness, large scale applicability, insensitivity to

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toxic substances and availability of various adsorbents made adsorption the most practical and economic technique for dyes removal [1, 7, 10, 11]. However, finding an efficient and low-cost adsorbent still the key of the adsorption process. Several low-cost materials were used either as adsorbent or as precursors for adsorbent preparation including natural materials (e.g. pinecones [12], algae[3], humic acids[13-15] and clay minerals [16] and industrial waste (e.g. spent pickle liquor [17], wool fiber waste[6]and nylon 66 fiber waste[18].

The textile industry is one of the most essential commodity goods industries. Textile recycling is supposed to give an answer to the finding low-cost adsorbent materials. The production of finished yarns, textiles, technical textiles, nonwovens and garments is accompanied with generation a large amount of pre-consumer textile waste causing a further serious disposal problem. For this reason, textile recycling is beneficial for environmental and economic reasons, such as reduction of landfill space, less energy consumption and reduce of wastewater [19-21].

Viscose is one of the most important and cheapest of all cellulosic fibers used in clothing manufacturing. Viscose is a linear cellulosic polymer, which is similar to cotton but without spiral configuration like cotton. Unlike cotton, viscose cellulosic polymer contains 60-65% amorphous and shorter polymers. On the contrary, Cotton has 65-70% crystalline region and 30- 35% amorphous cellulose. It is supposed to overcome the steadily increasing problems of higher world market cotton prices and cotton demand problem[22].

The current work aims to produce a low-cost sorbent for cationic dye depending on pre-consumer viscose fibers waste. To achieve this goal, selective oxidation treatment was carried out to viscose fiber waste at different conditions such as sodium periodate concentrations, time of treatment and time of further oxidation by sodium chlorite. Finally, both of unmodified and oxidized viscose fiber waste were physically modified by ball mill technique to obtain powder with high surface area to enhance the ability of dye adsorption. On the other hand, the adsorption performance of the physically and chemically modified waste viscose 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

Materials

Viscose fiber waste (VF) was provided by Misr Rayon (Cairo, Egypt). Sodium periodate was purchased from sigma-Aldrich (Merck), Germany. All chemicals and solvents used were reagent grade and used without further treatment or purification.

Methods

Purification of viscose fiber waste

The viscose fibers were purified in order to obtain a well-defined reference substance according to procedure described in the literature[23]. In brief, Removal of non-cellulose compounds (hemicellulose, waxes, pectin, proteins) by using boiling alkaline cleaning method followed by oxidative bleaching and demineralization to remove natural dyes, pigments and cations respectively.

Preparation of oxidized viscose fiber

Purified viscose fiber samples were oxidized according to literature procedure by immersing in solutions of sodium periodate in 0.1 M acetic buffer, pH 4.0, at different concentrations of sodium periodate in the range of 2.0, 3.0 and 4.0 mg/mL[24]. Subsequently, the mixture was then stirred in the dark at room temperature for 60, 150, and 360 min. After completion of the oxidation, the viscose fiber samples were washed thoroughly with ice-cold distilled water on a filter paper set in a Büchner funnel. Furthermore, the obtained aldehyde groups at C₂-C₃ were selectively oxidized to carboxyl groups with sodium chlorite 0.2 M at pH 5 for 24, 36 and 48 hrs. at room temperature. The oxidized fibers were washed with distilled water to constant conductivity and dried in air[25-27].

Powder preparation

Viscose fibers (VF), as well as oxidized viscose fibers (OVF), were both milled separately using the ball milling technique (Retsch PM 100, Germany), equipped with zirconium balls, to produce viscose powder (VP) and oxidized viscose powder (OVP). The total milling time was adjusted for 8 hours, stopped each 10 min for 5 min and then start over in a reverse direction[28].

Characterization

Determination of the carboxylic content

The carboxyl group content present in the oxidized viscose was measured according to the methylene blue method described in the literature[23]. The dye methylene blue binds to acid carboxylic groups of fibers using the principle of ion exchange. As the treatment, a weighted cellulose sample (approx. 0.5 g) was suspended in 25 ml of aqueous methylene blue chloride solution (300 mg/l) and 25 ml of borate buffer of pH = 8.5 for 1 h at 20 °C in a 100 ml Erlenmeyer flask and then filtered. Then 10 ml of 0.1 N HCl and subsequently water, up to 100 ml, were added and the methylene blue content of the liquid was determined photometrically, employing a calibration plot. The carboxyl group content of the sample is obtained according to Equation 1[]:

$$-\text{COOH group content} = \frac{(7.5 - A) \cdot 0.00313}{m} \text{ mmol/g} \quad (1)$$

where A is the total amount of free methylene blue [mg] and m is the weight of oven-dried sample[30].

Scanning electron microscope (SEM)

The morphological structure of viscose powder and the modified viscose were investigated with scanning electron microscopy. All samples were mounted on aluminum stubs, and sputter coated with gold in a 150 Å sputter (coated Edwards), and examined by Quanta FEG 250. Electron Probe Microanalysis (Japan) equipped with Energy-Dispersive X-ray facility (EDAX), magnification range 35-10,000, accelerating voltage 20 kV.

Adsorption studies.

The cationic thiazine methylene blue dye (MB) was used as adsorbate in this study. 1.00 g MB was dissolved in double distilled water to get a 1000 mg/L stock solution. Different working solutions were prepared by diluting the stock solution and their absorbance was measured by UV-visible spectrophotometer (Shimadzu UV-2600) at wavelength 664 nm. The absorbance values were plotted vs concentration to get a standard curve with R² = 0.99.

Batch adsorption experiments were performed at room temperature in 250 mL stopper conical flasks. A weight of the adsorbent was shocked at 120 rpm with a series of 100 mL MB solution. At definite times, sample was withdrawn, filtered, and the remaining MB concentration in the filtrate was measured as described above. The adsorption

percentage (%) and quantity of MB adsorbed per unit mass of the adsorbent (*q_t*, mg/g) was calculated by Eq. (2) and (3), respectively.

$$\text{Adsorption \%} = \left(1 - \frac{C_e}{C_o}\right) \times 100 \quad (2)$$

$$q_t = (C_o - C_t) \frac{V}{m} \quad (3)$$

Where *C_o*, *C_t* and *C_e* are the concentration (mg/L) of MB at zero-time, time t and equilibrium, respectively, V (L) is the volume of MB solution and m (g) is the amount of the adsorbent.

Adsorption kinetics were examined by mixing 0.3 g of the adsorbent with 100 mL MB solution (20 mg/L, original solution pH 6.5), shaking for predetermined time interval. The effect of adsorbent amount on the adsorption was studied by shaking different dosages; namely 1, 3, 5, 7, and 9 g/L, with 100 mL MB solution (20 mg/L, original solution) for 1 hrs (deduced for the kinetics study). Also, the effect of MB solution initial pH (pH_o) was investigated by adjusting the pH of MB solution (20 mg/L) to 3, 5, 7, and 9 using 0.1 M HCl or 0.1 M NaOH, shaking with 7 g/L of the adsorbent (deduced for the dosage effect study) for 1 h. Adsorption isotherms were obtained by shaking 7 g/L of adsorbent with MB solution of different concentrations (20–80 mg/L) adjusted to pH 9 (deduced from the pH effect study) for 60 min. The pseudo-first-order (Eq. (4)) and pseudo-second-order (Eq. (5)) kinetic models were used to simulate the adsorption kinetics and Freundlich (Eq. (6)), Langmuir (Eq. (7)) and Dubinin-Radushkevich (Eq. (8)) isothermal models were used to simulate the adsorption isotherms.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{1}{Q_o} C_e \quad (7)$$

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (8)$$

where *q_t* (mg/g) is the mass of MB adsorbed per gram of adsorbent at time, equilibrium *k₁* is the rate constant of the pseudo-first-order, *k₂* is the pseudo-second-order rate constant, *Q_o* is the theoretical maximum monolayer coverage capacity (mg/g) and *K_L* is Langmuir isotherm constant (L/mg), *K_f* is Freundlich isotherm constant (L/g), *n* is related

to adsorption intensity, q_m is D-R's monolayer capacity (mg/g), β is constant enables calculating the sorption energy ($\epsilon = \frac{1}{\sqrt{-2\beta}}$), and ϵ

($= \frac{RT \ln(1 + \frac{1}{c_e})}{\epsilon}$) R is the gas constant, and T is the absolute temperature (K)) is Polanyi potential.

Procedural blank and MB standard were analyzed routinely in each sample batch. Insignificant adsorption % was observed in the procedural blank. Each experiment was run in duplicate and the average data were presented.

Results and Discussion

Characterization

Carboxylic content

Carboxylic acid groups, -COOH, represent the ion exchange capacity of the modified viscose fiber, i.e., the ability to absorb cationic dyes during wastewater treatment, the values of the carboxyl group content obtained by the methylene blue method for different modified viscose fibers are presented in Table 1.

TABLE 1. Carboxylic content of chemically modified viscose fibers.

Sample [sodium periodate (mg/mL)/time of Reaction(min.)]	Carboxyl content after selective oxidation, mmol/Kg		
	24 hrs	36 hrs	48 hrs
2.0/60	30.28	34.16	38.02
2.0/150	32.15	35.36	39.15
2.0/360	35.36	37.32	40.00
3.0/60	44.19	46.72	48.63
3.0/150	42.15	45.36	49.15
3.0/360	45.36	47.32	50.00
4.0/60	54.12	56.07	57.10
4.0/150	54.08	55.26	57.00
4.0/360	54.63	55.12	56.60

[*-COOH group content*] of Reference sample is 27.18 mmol/Kg

It was noted that, the untreated samples possess a considerable number of the carboxyl groups, i.e. 27.18 mmol/kg. This can be explained by the pre-treatment process during viscose manufacturing which induces the formation of carboxyl groups. It was observed that, in the second step of selective oxidation the content of carboxyl groups increases with increasing the time of oxidation reaction. For instance, the carboxylic content of selective oxidized viscose fiber waste using sodium chlorite solution for 24, 36, and 48 hours were gradually increased from 45.36 to 47.32 mmol/kg and finally 50.00 mmol/kg respectively in case of using solution of sodium periodate 3.0 mg/mL for 360 min. This increasing in the carboxylic content could be explained by the first modification step of the aldehyde groups formed at the C2-C3 positions, and in a second reaction step these aldehyde groups are oxidized to carboxyl groups. Furthermore, it was observed that a slight increase in the carboxyl

groups appears after increasing the concentration of sodium periodate to 4.0 mg/mL for 60 min regardless the time of selective oxidation by sodium chlorite. Therefore, it was expected to increase the ion exchange capacity of the oxidized viscose fiber after the treatment process with 4.0 mg/mL of sodium periodate for 60 min, followed by the oxidation with sodium chlorite for 48 hrs, as the carboxylic content obtained at this reaction condition was about 110 % higher in comparison with the unmodified viscose fiber.

Surface morphology

The results for the methylene blue method for determination of carboxyl group content showed that the highest -COOH group content was observed in samples obtained by using sodium periodate for 60 min. followed by the oxidation with sodium chlorite for 36 hrs. therefore, this modified sample was milled against the unmodified viscose fiber. Figure 1 shows the

SEM of unmodified viscose powder and modified viscose powder. It indicated that both viscose powder (VP) and oxidized viscose powder (OVP) have different particle size. The milling process of viscose fibers at similar milling conditions leads to an increase in the specific surface area from (0.85 m²/g) to (241 m²/g) for VF and VP, respectively.

Adsorption performance

Effect of time. The adsorption kinetics determines the necessary time for the accomplishment of adsorption process. Figure 2 illustrates that adsorption is very fast process and OVP is more efficient adsorbent than VP. The amount of MB adsorbed by OVP is 1.18 times higher than VP. Also, for OVP, about 89 % of the equilibrium uptake was achieved in 5 minutes and the equilibrium was attained in 15 minutes with 78% of MB removed. While, for VP kinetics was some what sluggish, only 53 % of the equilibrium uptake was achieved in 5 minutes and the equilibrium was reached in 20 minutes with 67% of MB removed. These observations manifest the key role of the introduced carboxyl groups in the adsorption of MB.

Kinetics modeling. Figure 3 a and b displays the plots of the pseudo-first-order and pseudo-second-order models. The correlation coefficient (R²) and the calculated parameters for these models are provided in Table 2. It is noticeable that the pseudo-second-order model gives the best fit for the kinetic data of both VP and OVP according to the R² value and the similarity between the calculated and experimental values

of MB equilibrium uptake. Therefore, the results of the pseudo-second-order model will be further discussed.

Comparing the k_2 values indicates that the adsorption rate of OVP is considerably higher (7.2 times) than VP. On the other hand, comparing the $q_{e(cal)}$ values of VP and OVP indicate that OVP adsorbs slightly or relatively higher amount of MB. However, OVP still superior than the VP owing to the significantly higher adsorption rate as indicated by the k_2 values. The adsorption rate is critical factor as it directly affects the time of contaminated water treatment. Noteworthy that the value of $q_{e(cal)}$ for OVP was slightly deviated from the $q_{e(exp)}$. Finally, fitting the kinetics data to the pseudo-second-order model implies that the rate of adsorption might be ruled by chemical interactions between the adsorbent surface functional groups and MB molecules [3].

Effect of dosage. Figure 4 shows that dosage has significant effect on MB adsorption, especially up to dosage of 7 g/L. As seen in Fig. 4, the MB adsorption % by OVP increases from 48 to 91, a bit higher than the adsorption % of VP (32 to 84), with an increase in dosage from 1 to 7 g/L. This might be caused by increasing the number of adsorption sites available for MB [3, 6, 13]. At dosage higher than 7 g/L, the increase in dosage, consequently adsorption sites, has insignificant effect on the adsorption %. This possibly owing to approaching 100% removal. Accordingly, 7 g/L was considered adequate to achieve high MB adsorption % and was selected as the optimum dosage hereafter.

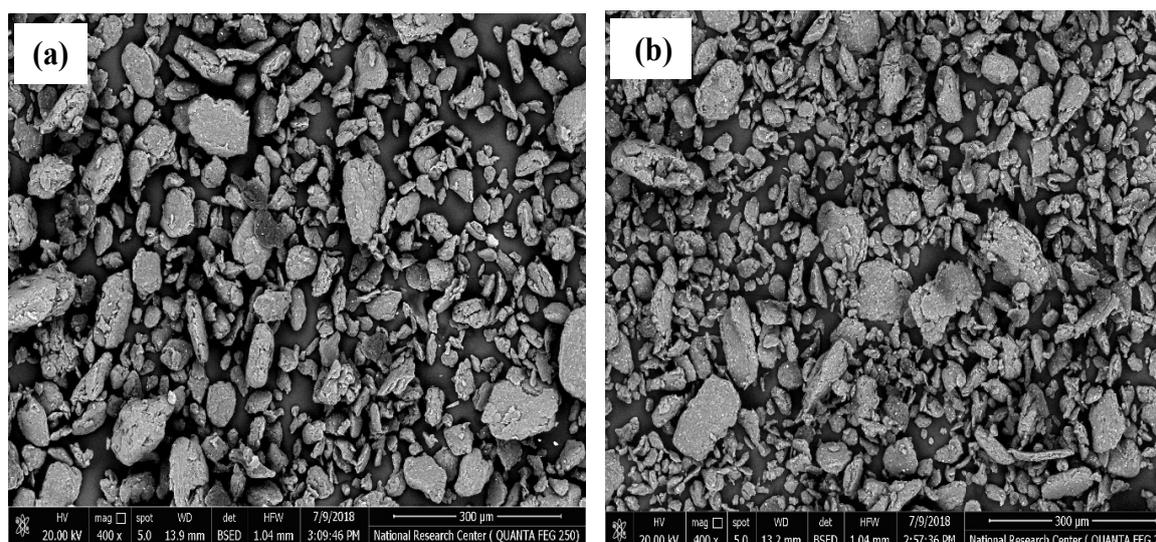


Fig. 1. SEM of (a) unmodified viscose powder and (b) modified viscose powder with carboxyl content 57.10 mmol/Kg.

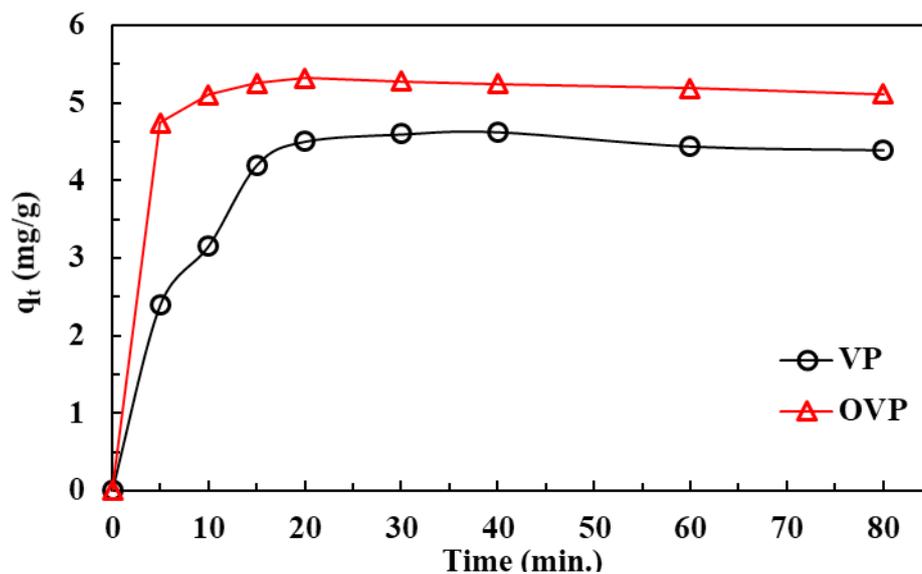


Fig. 2. Variation of mass adsorbed of MB per unit mass of adsorbent as a function of contact time. $C_o = 20$ mg/L, dosage = 3 g/L, and pH = 6.5.

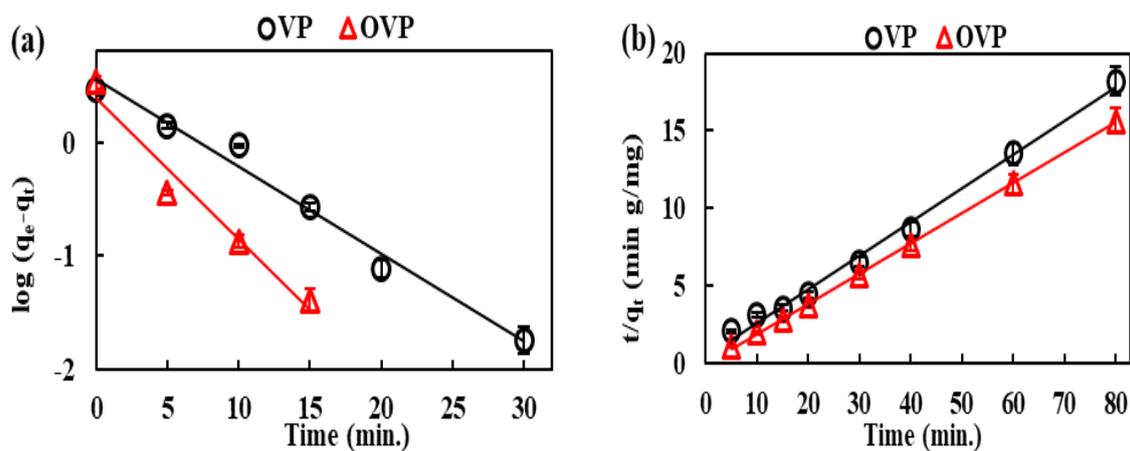


Fig. 3. (a) Pseudo-first-order and (b) Pseudo-second-order plots for the MB adsorption onto VP and OVP.

TABLE 2. Calculated kinetic models' parameters.

Kinetic model	Parameter	VP	OVP
	$q_{c(\text{exp})}$	4.63	5.31
Pseudo-first-order	R^2	0.98	0.96
	k_1	0.18	0.29
	q_c	5.60	3.82
Pseudo-second-order	R^2	0.99	0.99
	k_2	0.10	0.72
	q_c	4.62	5.14

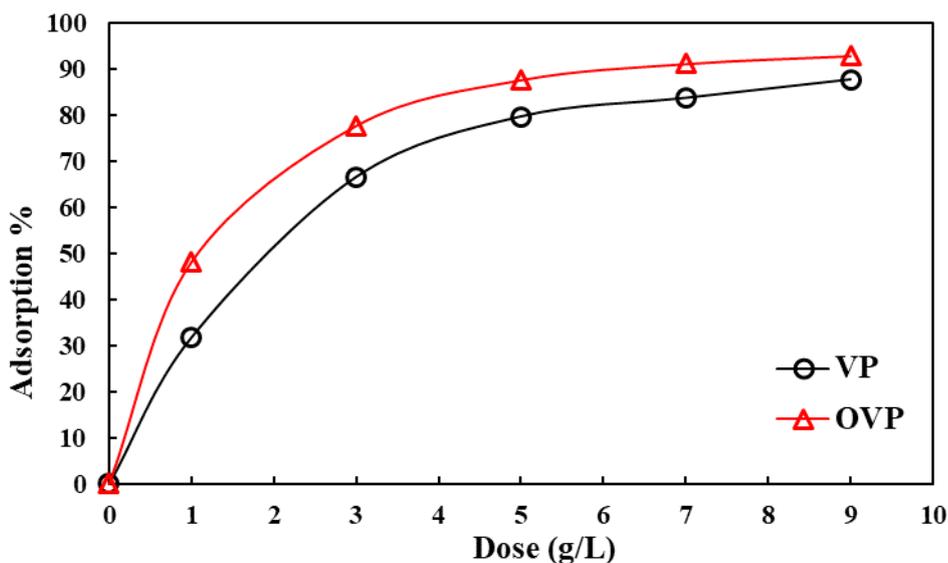


Fig. 4. Variation of MB adsorption percentage as a function of dosage. $C_o = 20$ mg/L, contact time = 1 hrs, and pH = 6.5.

Effect of solution initial pH. The effect of MB solution initial pH on MB adsorption % is shown in Fig. 5. Both VP and OVP show little adsorption at pH 3. The extent of adsorption increased at pH 5 – 7 and peaked at pH 9. Under acidic conditions the competition exerted by H_3O^+ reduces the MB adsorption. At low pH values the concentration of H_3O^+ is high thus the adsorption reduction is more pronounced. As the pH increased the concentration of H_3O^+ decreases, therefore the

competition between H_3O^+ and MB decreases and the MB adsorption % increases [31]. On the other hand, the surface of the adsorbents contains functional groups which deprotonate gradually as the pH increased. Thus more MB are adsorbed via the electrostatic interactions between the negative charges of the deprotonated functional groups and the cationic dye MB [3, 6, 31]. Based on these results, the optimal solution initial pH was selected to be 9.

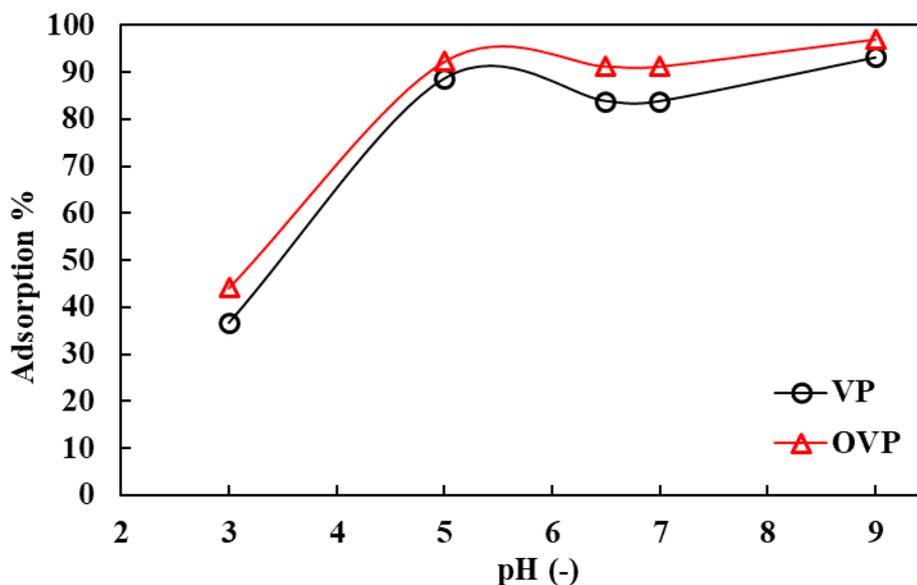


Fig. 5. Variation of MB adsorption percentage as a function of pH. $C_o = 20$ mg/L, contact time = 1 hrs, and dosage = 7 g/L.

Effect of initial MB concentration. The amount of MB adsorbed onto VP and OVP at different initial concentrations is shown in Fig. 6 a. Larger amount of MB was adsorbed when the initial concentration of the MB increased. As the initial concentration increases there will be more MB molecules in the aqueous phase consequently the chances of interaction with the adsorbents increase. Also, as the initial concentration increases, the concentration gradient increases and consequently, the driving force for mass transfer to the adsorbent surface [31-33].

Isotherm modeling. The isotherms data was fitted to the widely used isothermal models, Langmuir, Freundlich, and Dubinin-Radushkevich isotherms. Plots of the linear forms of these models are shown in Fig. 6b, c, and d, respectively, and the values of the calculated isotherms parameters are presented in Table 3.

The results show that, among other models, the correlation coefficient of Langmuir model was the highest. Which indicate that Langmuir model fitted better to the adsorption data, suggesting the formation of monolayer of MB onto the surface of adsorbents which has a homogeneous and fixed number of energetically equal adsorption sites[15, 31, 34, 35].

Equation 9 was used to calculate the key characteristic of Langmuir model called equilibrium parameter (R_L).

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

The value of R_L tells about the nature of adsorption process either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$)[15]. The values of R_L in Table 3 indicate the favorability of the adsorption process.

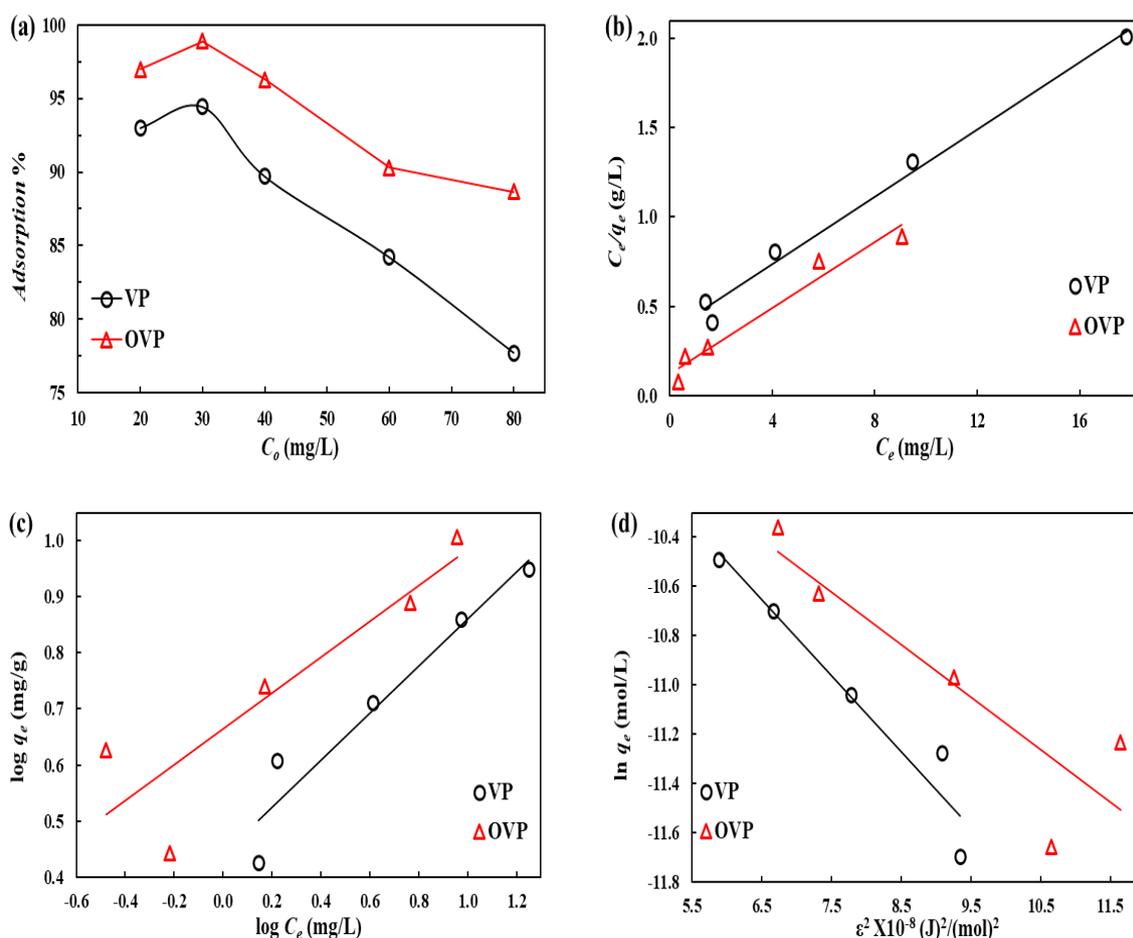


Fig. 6. Effect of initial MB concentration on the adsorption efficiency (a) and linear plots of (b) Langmuir, (c) Freundlich, and (d) Dubinin-Radushkevich models.

TABLE 3. Calculated isotherm models' parameters.

Isothermal model	Parameter	VP	OVP
Langmuir	R^2	0.99	0.96
	Q_o	10.60	10.93
	K_L	0.26	0.73
	R_L	0.06 – 0.16	0.02 – 0.06
Freundlich	R^2	0.93	0.80
	K_f	2.76	4.62
	$1/n$	0.42	0.32
Dubinin-Radushkevich	R^2	0.94	0.79
	E	12.75	15.30

Conclusions

In this work, viscose waste fibers (VP) were modified by selective oxidation to improve the ability of adsorbing cationic dyes during waste water treatment. For this purpose, different treatment parameters were investigated such as sodium periodate concentration, and time of selective oxidation with sodium chlorite. The content of carboxyl groups obtained by 4.0 mg/mL of sodium periodate for 60 min, followed by the oxidation with sodium chlorite for 24 hrs is about 110 % higher in comparison with unmodified viscose fiber. Moreover, the surface area was increased from (0.85 m²/g) to (241 m²/g) for VP and OVP, respectively by ball milling technique. The efficiency of VP and OVP for the adsorptive removal of MB as a model for cationic dyes was studied in detail. The effects of contact time, dosage of adsorbents, and MB solution initial pH and concentration were investigated. About 84% of MB was removed using 7 g/L of VP and the percentage removal increased to about 91% using OVP. Alkaline pH favors the MB removal; 93% and 97 % of MB were removed at pH 9 using VP and OVP, respectively. The adsorption kinetics followed the pseudo-second-order equation implying that the adsorption is a chemisorption process. Langmuir model was the best model to describe the adsorption isotherm and indicated that the adsorption process is favorable and includes the formation of monolayer of MB onto the surface of VP and OVP.

References

- Zhang C., Li Y., Li Y., Zhang W., Wang X., He X., Yu M., Synthesis and Zn(II) modification of hierarchical porous carbon materials from petroleum pitch for effective adsorption of organic dyes, *Chemosphere*, **216**, 379-386. (2019).
- Tanhaei B., Ayati A., Sillanpää M., Magnetic xanthate modified chitosan as an emerging adsorbent for cationic azo dyes removal: Kinetic, thermodynamic and isothermal studies, *International Journal of Biological Macromolecules*, **121**, 1126-1134. (2019).
- Ghafar H.H.A., Embaby M.A., Radwan E.K., Abdel-Aty A.M., Biosorptive removal of basic dye methylene blue using raw and CaCl₂ treated biomass of green microalga *Scenedesmus obliquus*, *Desalination and Water Treatment*, **81**, 274-281. (2017).
- Guan Y., Xia M., Wang X., Cao W., Marchetti A., Water-based preparation of nano-sized NH₂-MIL-53(Al) frameworks for enhanced dye removal, *Inorganica Chimica Acta*, **484**, 180-184. (2019).
- Qi Z.-P., Kang Y.-S., Guo F., Sun W.-Y., Controlled synthesis of NbO-type metal-organic framework nano/microcrystals with superior capacity and selectivity for dye adsorption from aqueous solution, *Microporous and Mesoporous Materials*, **273**, 60-66. (2019).
- Ghafar H., Salem T., Radwan E., El-Sayed

- A.A., Embaby M., Salama M., Modification of Waste Wool Fiber as Low Cost Adsorbent for The Removal of Methylene Blue from Aqueous Solution, *Egyptian Journal of Chemistry*, **60**, 395-406. (2017).
7. El-Naggar M.E., Radwan E.K., El-Wakeel S.T., Kafafy H., Gad-Allah T.A., El-Kalliny A.S., Shaheen T.I., Synthesis, characterization and adsorption properties of microcrystalline cellulose based nanogel for dyes and heavy metals removal, *International Journal of Biological Macromolecules*, **113**, 248-258. (2018).
 8. Radwan E.K., Kafafy H., El-Wakeel S.T., Shaheen T.I., Gad-Allah T.A., El-Kalliny A.S., El-Naggar M.E., Remediation of Cd(II) and reactive red 195 dye in wastewater by nanosized gels of grafted carboxymethyl cellulose, *Cellulose*, **25**, 6645-6660 (2018).
 9. Chaari I., Fakhfakh E., Medhioub M., Jamoussi F., Comparative study on adsorption of cationic and anionic dyes by smectite rich natural clays, *Journal of Molecular Structure*, **1179**, 672-677. (2019).
 10. Noorimotlagh Z., Mirzaee S.A., Martinez S.S., Alavi S., Ahmadi M., Jaafarzadeh N., Adsorption of textile dye in activated carbons prepared from DVD and CD wastes modified with multi-wall carbon nanotubes: Equilibrium isotherms, kinetics and thermodynamic study, *Chemical Engineering Research and Design*, **141**, 290-301 (2019).
 11. de Mattos N.R., de Oliveira C.R., Camargo L.G.B., da Silva R.S.R., Lavall R.L., Azo dye adsorption on anthracite: A view of thermodynamics, kinetics and cosmotropic effects, *Separation and Purification Technology*, **209**, 806-814. (2019).
 12. Radwan E.K., El-Wakeel S.T., Gad-Allah T.A., Effects of activation conditions on the structural and adsorption characteristics of pinecones derived activated carbons, *Journal of Dispersion Science and Technology*, (2018).
 13. Radwan E.K., Ghafar H.H.A., Moursy A.S., Langford C.H., Bedair A.H., Achari G., Adsorptive removal of hazardous organic water pollutants by humic acid-carbon hybrid materials: kinetics and isotherm study, *Desalination and Water Treatment*, **80**, 297-305. (2017).
 14. Radwan E.K., Ghafar H.H.A., Moursy A.S., Langford C.H., Bedair A.H., Achari G., Preparation and characterization of humic acid-carbon hybrid materials as adsorbents for organic micro-pollutants, *Environmental Science and Pollution Research*, **22**, 12035-12049 (2015).
 15. El-Wakeel S.T., Radwan E.K., Ghafar H.H.A., Moursy A.S., Humic acid-carbon hybrid material as lead (II) ions adsorbent, *Desalination and Water Treatment*, **74**, 216-223. (2017).
 16. Embaby M.A., Ghafar H.H.A., Shakhdofo M.M.E., Khalil N.M., Radwan E.K., Removal of iron and manganese from aqueous solution using some clay minerals collected from Saudi Arabia, *Desalination and Water Treatment*, **65**, 259-266. (2017).
 17. El-Wakeel S.T., Radwan E.K., El-Kalliny A.S., Gad-Allah T.A., El-Sherif I.Y., Structural, Magnetic and Adsorption Characteristics of Magnetite Nanoparticles Prepared from Spent Pickle Liquor, *International Journal of Chemtech Research*, **9**, 373-382 (2016).
 18. Metwally B.S., Atef El-Sayed A., Radwan E.K., Hamouda A.S., El-Sheikh M.N., Salama M., Fabrication, characterization, and dye adsorption capability of recycled modified polyamide nanofibers, *Egyptian Journal of Chemistry*, **61**, 867-882. (2018).
 19. Ratanakamnuan U., Atong D., Aht-Ong D., Cellulose esters from waste cotton fabric via conventional and microwave heating, *Carbohydrate Polymers*, **87**, 84-94. (2012).
 20. Di Y., Long G., Zhang H., Li Q., Preparation and Properties of Viscose Rayon/O-carboxymethyl Chitosan Antibacterial Fibers, *Journal of Engineered Fibers and Fabrics*, **6**, 39-43. (2011).
 21. Rani S., Jamal Z., Recycling of textiles waste for environmental protection, (2018).
 22. Ramachandran T., Thirunarayanan A., Overview and significance of viscose yarn quality characteristics and suggestive process to improve it.
 23. Fras L., Stana-Kleinschek K., Ribitsch V., Sfiligoj-Smole M., Kreze T., Quantitative determination of carboxyl groups in cellulose by complexometric titration, *Lenzinger Berichte*, **81**, 80-88. (2002).
 24. He H., Hou X., Ma B., Zhuang L., Li C., He S., Chen S., The oxidation of viscose fiber optimized by response surface methodology and its further amination with PEI for CO₂ adsorption, *Cellulose*, **23**, 2539-2548. (2016).
 25. Kumar V., Yang T., HNO₃/H₃PO₄-NANO₂

- mediated oxidation of cellulose—preparation and characterization of bioabsorbable oxidized celluloses in high yields and with different levels of oxidation, *Carbohydrate Polymers*, **48**, 403-412. (2002).
26. Saito T., Isogai A., TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions, *Biomacromolecules*, **5**, 1983-1989. (2004).
27. Praskalo J., Kostic M., Potthast A., Popov G., Pejic B., Skundric P., Sorption properties of TEMPO-oxidized natural and man-made cellulose fibers, *Carbohydrate Polymers*, **77**, 791-798. (2009).
28. Atef El-Sayed A., Salama M., Kantouch A.A.M., Wool micro powder as a metal ion exchanger for the removal of copper and zinc, *Desalination and Water Treatment*, **56**, 1010-1019. (2015).
29. Šaupperl O., Stana-Kleinschek K., Differences between cotton and viscose fibers crosslinked with BTCA, *Textile Research Journal*, **80**, 383-392. (2010).
30. Klemm D., Philipp B., Heinze T., Heinze U., Wagenknecht W., Comprehensive cellulose chemistry. Volume 1: *Fundamentals and Analytical Methods*, Wiley-VCH Verlag GmbH, (1998).
31. Wang Y., Wang X., Ding Y., Zhou Z., Hao C., Zhou S., Novel sodium lignosulphonate assisted synthesis of well dispersed Fe₃O₄ microspheres for efficient adsorption of copper (II), *Powder Technology*, **325**, 597-605. (2018).
32. Iriel A., Bruneel S.P., Schenone N., Cirelli A.F., The removal of fluoride from aqueous solution by a lateritic soil adsorption: Kinetic and equilibrium studies, *Ecotoxicology and Environmental Safety*, **149**, 166-172. (2018).
33. Khanday W.A., Hameed B.H., Zeolite-hydroxyapatite-activated oil palm ash composite for antibiotic tetracycline adsorption, *Fuel*, **215**, 499-505. (2018).
34. Melo B.C., Paulino F.A.A., Cardoso V.A., Pereira A.G.B., Fajardo A.R., Rodrigues F.H.A., Cellulose nanowhiskers improve the methylene blue adsorption capacity of chitosan-g-poly(acrylic acid) hydrogel, *Carbohydrate Polymers*, **181**, 358-367 (2018).
35. Singh T., Singhal R., Reuse of a waste adsorbent poly(AAc/AM/SH)-Cu superabsorbent hydrogel, for the potential phosphate ion removal from waste water: Matrix effects, adsorption kinetics, and thermodynamic studies, *Journal of Applied Polymer Science*, **129**, 3126-3139. (2013).

إعادة تدوير مخلفات ألياف الفسكوز لإزالة الصبغات القاعدية من المحلول المائي

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إعادة تدوير المخلفات النسيجية جذبت اهتماما بالغا لتصنيع ممتزات الصبغات ذات السعر المنخفض لإزالة الصبغات من المحاليل المائية. وقد تعتبر الألياف السيلولوزيه المكون الأساسي في مخلفات الفسكوز الحل الأمثل لإيجاد مواد ممتزة جديدة ذات سعر منخفض. وفي هذا البحث، تم تحويل مخلفات الياف الفسكوز عن طريق الأكسدة الانتقائية وذلك لتحسين قدرتها على امتزاز الأصباغ القاعدية أثناء معالجة مياه الصرف. ومن أجل هذا الغرض، تمت دراسة الظروف المختلفة لعملية الأكسدة مثل تركيز بيرايودييد الصوديوم، ووقت الأكسدة الانتقائية مع كلوريت الصوديوم. بعد ذلك، تم طحن كل من ألياف الفسكوز غير المؤكسده والمؤكسده لإنتاج مسحوق فسكوزي غير مؤكسد ومسحوق فسكوزي مؤكسد. تمت دراسة الخصائص السطحية لمساحيق الفسكوز باستخدام المجهر الإلكتروني. كما تمت الدراسة الحركية لامتزاز صبغه الميثيلين الأزرق على سطح مساحيق ألياف الفسكوز غير المؤكسده ومساحيق ألياف الفسكوز المؤكسده كدالة لوقت الالتصاق (٠-٨٠ دقيقة)، جرعة المادة الممتزة (١-٩ جم / لتر)، والاس الهيدروجيني الأولي لمحلول الصبغة (٣-٩) والتركيز الأولي لصبغه الميثيلين الأزرق (٢٠-٨٠ مجم / لتر). وقد أظهرت النتائج أن عملية امتزاز الصبغة القاعدية على كلا من مساحيق الياف الفسكوز المؤكسد والغير مؤكسد هي عملية سريعة ومواتية ويمكن توصيفها بشكل جيد بواسطة استخدام نموذج Langmuir. وأوضحت النتائج وجود ارتباط بين ارتفاع قدرة امتزاز مساحيق الياف الفسكوز المؤكسده عن غيرها الغير مؤكسده وزيادة مجموعات الكربوكسيل المتكونة نتيجة عملية الأكسدة. وقد توصلت الدراسة الي امكانيه استخدام مساحيق ألياف الفسكوز المؤكسده كمتزات لصبغات قاعديه رخيصة السعر لمعالجة مياه الصرف.