



Dyeing of Waste Cotton Fabric as Biosorbent of Heavy Metals from Aqueous Solution

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Abstract

Heavy metal pollution is a major problem in the environment. The impact of toxic metal ions can be minimized by different technologies. But among them, adsorption was found to be very efficient and common due to the low concentration of metal uptake and economically feasible properties. Cotton fabrics are of low cost and widely used, and very promising for the future. These are available in abundant quantity, are cheap and have low or little economic value. Waste cotton fabrics (WCF) are used in different metal detoxifications in water and waste water as adsorbent for the sorption of Ca (II) and Mg (II) ions from aqueous solution. The cotton fabrics were characterized by before and after the adsorption process. Cotton fabric has been used in two directions removal of heavy metals and dyeing. The results of maximum adsorption capacity was 42 mg g⁻¹ for Ca (II) and 35 mg g⁻¹ for Mg (II) at optimal pH (11). The dyeing behavior of the WCF before and after adsorption of metals (WCF-Ca (II)) with reactive yellow 145 (RY 145) has been studied and the build up of dye, measured as exhaustion percentage (E%) and (K/S). The overall fastness properties to light, perspiration, washing for the colored samples are ranging from very good to excellent. In this study shows significant benefit of eco-friendly and cost-efficiency for removal of metals in potential river metal pollutions comparing with traditional adsorbents.

Keywords: Waste cotton fabric, Reactive yellow 145, Heavy metal ions, sorption process, dyeing process.

1. Introduction

The major metal polluting industries are tannery, electroplating, textile, fertilizer, pesticide and metal processing industries as well as mining sectors. These toxic metals are major pollutants of freshwater reserves [1]. Most of the metals are non-biodegradable, highly toxic and carcinogenic in nature. Toxic heavy metals reach through various food chains and cause toxic effects on the ecosystem as well as humans and animals. Therefore, it is necessary to treat metal-contaminated wastewater before its discharge into the environment.

A number of technologies are available to treat heavy metal-laden wastewater. Among them, some popular techniques are chemical precipitation [2], ion exchange [3], adsorption [4-6], nanofiltration [7-10] and electrochemical process [11,12]. Comparatively, the adsorption process seems to be a significant technique due to its wide applications, such as ease of operation, economical feasibility, wide availability

and simplicity of design [13]. Therefore, development of new approaches with simplicity, low cost and high-efficiency has great significance in theory and practice for treatment of heavy metal wastewater [14]. In recent years, various adsorbents are used to sorption heavy metal ions in polluted water [15]. Waste cotton fabric is considered as the efficient adsorbent and most widely applied in the sorption of heavy metal ions from water and low-cost adsorbents [16-19] and investigated the effect of pH, temperature, contact time, initial concentration and adsorbent doses. The application of cellulose-derived cotton wastes for a wide range of applications, such as environmental including dyes and heavy metal remediation from wastewater, Polymers geotechnical, packaging, and biomedical applications, with the potentials of forming composites [20].

Nowadays reactive dyes are widely used in dyeing cotton materials. It reacts with fiber in presence of alkali and adheres as a part of fiber. Here

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the dye contains a reactive group and this reactive group makes covalent bond with the fiber polymer and act as an integral part of fiber. This covalent bond is formed between the dye molecules and the terminal –OH (hydroxyl) group of cellulosic fibers on between the dye molecules [21].

In the conventional dyeing process of waste cotton fabric, a large amount of energy and a large quantity of salt are consumed causing fabric damage, pollution of rivers and streams, and upsetting the biological equilibrium. On the contrary, the treatment of waste cotton fabric with metal ion before dyeing process proved to be more rapid, uniform, efficient, while also increasing the dye affinity and improving the fastness properties of waste cotton fabric towards washing, light, rubbing and perspiration. It is considered a better alternative to the conventional dyeing technique due to the reduction of environmental impact, and energy consumption [22].

In this review, the potential of waste cotton adsorbent materials for various heavy metal uptake capacities was reported. And then waste Cotton fabric after adsorption process is used in dyeing for environmental benefits.

2. Materials and Methods

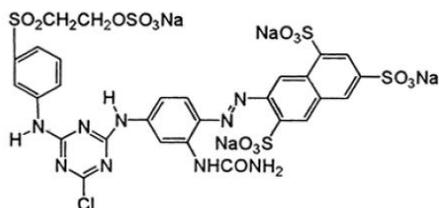
2.1. Material :

2.1.1 Waste Cotton fabric:

Waste Cotton fabric (WCF) was supplied by men's vest used as adsorbent for sorption of heavy metal ions as Ca (II) and Mg (II) from waste water.

2.1.2 Reactive dye :

Reactive dye used to study the dyeing process was C.I. Reactive yellow 145 Molecular formula ($C_{28}H_{20}ClN_9Na_4O_{16}S_5$) RY 145, were supplied from Imperial Chemical Industries (ICI) the chemical structure of RY 145 was shown below:



C.I. Reactive Yellow 145 (RY 145)

2.1.3 Chemicals :

NaOH, $CaSO_4$, $MgSO_4$, Na_2SO_4 and Na_2CO_3 All chemicals used, were purchased with high purity from Merck Darmstad, Germany. Bi distilled water was used throughout the experiments for preparation and dilution of the solutions. UV-visible spectrophotometer ((Model T60 spectrophotometer, United Kingdom)) was used to measure the absorbance of dyes to establish its λ_{max} and its concentration. pH of an aqueous solution

was measured by pH meter (WTW, Germany). For agitation of solutions, a shaker was used (IKA-KS 501, Germany and water bath for dyeing process.

2.2 Methods :

2.2.1 Adsorption experiments for single metal ion by cotton fabric :

WCF were washed with water to remove the adhering dirt then dried in an oven at 70°C for 6 h. After drying, they were cut with dimensions 1x1cm. WCF were pretreated with 0.1 M (NaOH) solution at boiling temperature for 20 min in order to increase hydrophilicity of WCF, then washed with distilled water until all sodium hydroxide was removed. After washing, they were dried in oven at 70°C for 6 h and then keep to further investigation for this study.

Experimental Techniques of metal sorption

sorption experiments were conducted in batch mode to evaluate the effect of various parameters, such as adsorbent dose the range of (0.5, 1, 1.5, 2, 2.5, 3 and 3.5g), pH of solution changed from (2 to 12) and initial metal concentration (0.5, 1, 3, 5, 7, 9, 15, 20, 25, 30 and 40 mg/L) on the sorption of Ca (II) and Mg (II) on WCF as adsorbent. sorption experiments were performed by known weight of adsorbents WCF (1g) were immersed in 40 ml of an aqueous metal Ca (II) and Mg (II) solutions in 50 ml stopper bottle maintained at 25°C for about 24h and the mixture was shaken at a constant agitation speed (200 rpm) for 30 min. The solution was separated from the mixture and analyzed for Ca (II) and Mg (II) concentration. from the preliminary experiments it had been found that the equilibrium was reached within the period of for all cases. The initial concentration of metal was about (0.5 mg/L) in all experiments, except for that carried out to examine the effect by the initial concentration of metal. The amount of metal sorption was calculated based on the difference of metal concentration in the aqueous solution were determined before and after the sorption by using atomic instrument. The amount of metal ions adsorbed per unit mass of the adsorbent was calculated using the following relationships [23]:

$$q_e = \frac{[C_0 - C_e]V}{M} \quad (1)$$

and the percent sorption may be calculated as:

$$\text{Sorption \%} = \left[\frac{(C_0 - C_e)}{C_0} \right] 100 \quad (2)$$

Where q_e (mg/g) amount of metal ions adsorbed per unit mass of the adsorbent (mg/g), C_0 is the initial concentration of metal ions in solution (mg/L) and C_e is the final metal ions concentration in aqueous solution after phase separation (mg/L) at any time, V is the volume of the solution (ml) and M is the weight of the WCF adsorbent used in (g).

Optimization of operational variables

The sorption process of Ca (II) and Mg (II) metal ions on the surface of WCF as adsorbents affected by several parameters such as effect of adsorbent dose, pH of solution, initial metal concentration and contact time have been examined. Adsorption isotherm and Kinetics studies by batch method [24] for the sorption of Ca (II) and Mg (II) under the given condition have also been investigated.

2.2.2 Dyeing procedures of WCF before and after sorption of metal with RY145 :

WCF and WCF-Ca(II) were dyed with RY 145 by applying batch technique under the dyeing recipe: dye concentration 10×10^{-3} g/l, Liquor ratio (LR) 1 : 100, pH 10, sodium sulphate (SS) 50 g/l, sodium carbonate (SC) 25 g/l, time 120 (min) and temperature 50,60,70,80,90 °C. At the end of dyeing, both the initial and equilibrium dye bath concentrations were measured with an UV-vis spectrophotometer at $\lambda_{\text{max}} = 423$ nm, to be ready for calculation of the percentage of dye exhaustion (E%). The dyed samples were removed, and rinsed in distilled water to remove the loosely fixed dye on the surface of dyed fabric, and were allowed to dry in the open air to be ready for the determination of cotton fabric properties. The percentage of dye exhaustion (E%) was calculated by using the equation:

$$E \% = C_0 - C_e / C_0 \times 100$$

(3)

where C_0 is the initial dye concentration, C_e is the dye concentration at equilibrium

2.2.3 Surface Characterization :

Field Emission Scanning Electron Microscope (FE-SEM) on a Quanta FEG 250 Czech Republic electron microscope and Fourier Transform Infrared spectroscopy (FTIR) rang of $4000-400 \text{ cm}^{-1}$ were recorded on JASCO FTIR 6100, 64scans with 4 cm^{-1} resolution using KBr pellets. Measurements were used for surface characterization

2.2.4 Determination of cotton Fabric Properties:

Color Fastness properties:

The dyed cotton samples at dyeing recipe were tested for various fastness properties such washing, light and perspiration according to ISO standard test methods [25]

3. Results and Discussion :

3.1 Characterization of the adsorbent :

3.1.1 SEM analysis :

The morphology features of WCF and WCF-Ca (II) were investigated using scanning electron microscopy (SEM). The SEM images of WCF and WCF-Ca (II) were shown in Figure 1(a,b) The WCF performed the smoother morphology of the surface under different magnification. The morphological structure of WCF-Ca (II) specimen revealed a harsh

and more crumple fiber surface relative to the control fabric [26].

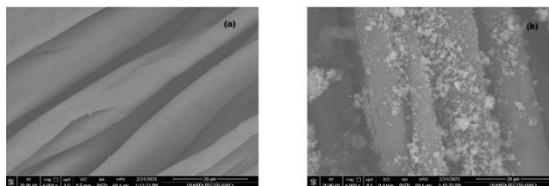


Fig. 1 : SEM image of (a) WCF (b) WCF-Ca (II)

3.1.2 FTIR spectrum analysis:

FTIR spectroscopy was used to analyze the major characteristic functional groups of the materials. FTIR spectra of WCF and WCF-Ca (II) were shown in Figure (2 a). In the spectrum of WCF, it was observed that the absorption peaks at approximately $1060-1150 \text{ cm}^{-1}$, $1250-1410 \text{ cm}^{-1}$, 2898 cm^{-1} , and $3600-3100 \text{ cm}^{-1}$ were assigned to the vibration of C–O (stretching), O–H (bending), C–H (stretching), and O–H (stretching) [27]. The adhesion of metal to the WCF was recorded and compared with the WCF as shown in figure (2 b) In the spectrum of WCF-Ca (II), the new peaks at $400-500 \text{ cm}^{-1}$ was assigned to the characteristic peak for metal ions Ca(II), Mg(II). The FTIR spectra ensure that metal were loaded onto the WCF successfully.

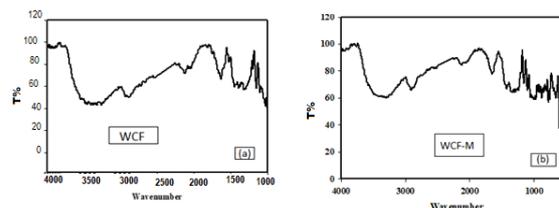


Fig. 2: FTIR spectra of (a) WCF and (b) WCF-Ca (II) .

3.2 Sorption parameters study of metal ions (Ca (II) and Mg (II)) by WCF :

The results obtained from 3D experimental runs conducted to observe the effect of the four adsorption factors (solution pH, initial dye concentration, adsorbent dose and time) using WCF as adsorbent. In this section the interaction effects of the four factors on the (% sorption) of metal ions are discussed in detail. The analyses are supported by the 3D plots of the interaction effects of the four factors on the percentage sorption of metal ions.

The interaction effect of solution pH and initial dye concentration.

The plot for combined effect of the solution pH and metal ions concentration. Figure (3) Suggests that increasing metal ions concentration results in a decreasing sorption of the metal ions, whereas, it increases with increase the pH value [28,29]. Ascending trend in metal sorption with increasing pH may be attributed to the negative charges on the metal ions molecules in the basic medium, from

figure, it can be seen that at high pH value (pH 11) more than 42% of Ca (II) and 35% Mg (II) percent in the solution were removed onto WCF adsorbent. The presence of these negative charged functional groups will also increase the percentage removal due to the attraction of the positive charged metal ions by the negatively charged surface functional groups. This behavior can be understood as the increasing adsorbate concentration with fixed adsorbent dose would result in saturation of the binding sites on the surface and subsequently declining of the adsorbate uptake with increasing concentration. The increasing pH increased the density of negative charge on the surface, which was contribute to the higher adsorption capacity.

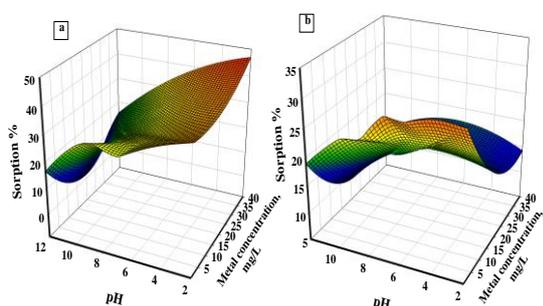


Fig. 3 : The three-dimensional response surfaces representing the combined effect of adsorbent dose and pH on adsorption of the (a) Ca (II) and (b) Mg (II) at contact time 40 min.

The interaction effect of solution pH and contact time

The 3D surface plot for combined effect of pH and contact time Figure (4) Shows at higher pH, the metal ions sorption increases with increasing contact time as the time of adsorption increases, metal ions % sorption increase [30,31]. This result indicates that both adsorption factors have significant effect on the % sorption of Ca (II) and Mg (II).

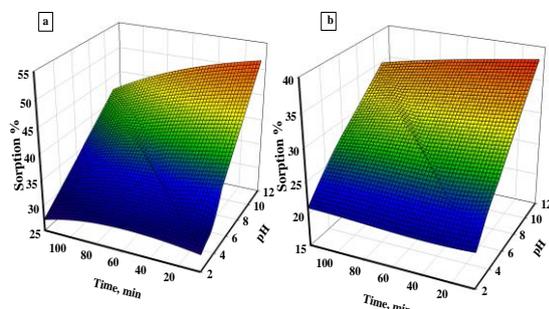


Fig 4 : 3D plot the interaction effect of pH of solution and contact time on sorption of (a) Ca (II) and (b) Mg (II) onto WCF.

The interaction effect of WCF adsorbent dose and metal ions concentration

The combined effect of WCF adsorbent dose and metal ions concentration on sorption of Ca (II) and Mg (II) in 3D surface plot is shown in Figure (5). It may be noted that the metal ions sorption increased with increasing adsorbent dose and decreasing metal ions concentration. This is due to increase in metal ions concentration, adsorption sites, surface area of the adsorbent are saturated, resulting in decrease in the adsorption efficiency.

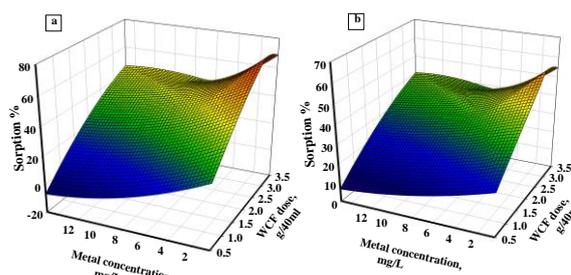


Fig. 5 : 3D plot the interaction effect of WCF adsorbent dose and metal ions concentration (a) Ca (II) and (b) Mg (II) onto WCF.

The interaction effect of adsorbent dose and contact time

Figure (6) shows the interactive influence of WCF adsorbent dose and contact time on the metal ions sorption from aqueous phase. It is evident that the metal ions sorption increased with the increase in both the adsorbent dose and contact time. The observed trend may be understood the increase in adsorbent dose would make higher number of adsorption sites available.

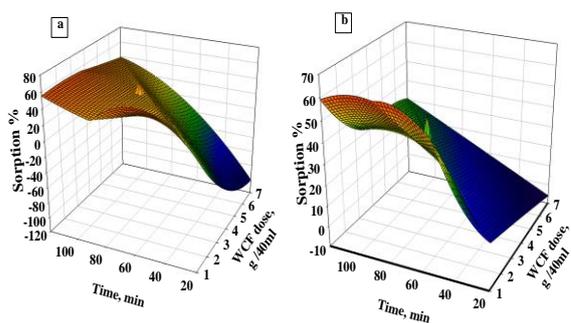


Fig. 6 : 3D plot the interaction effect of contact time and adsorbent dose on sorption of (a) Ca (II) and (b) Mg (II) onto WCF.

The interaction effect of metal ions concentration and contact time

The interactive effect of metal ions concentration and contact time on metal ions sorption is shown in 3D surface plot in Figure. (7). However beyond time 40 min for both metal by WCF, increasing the adsorption time has no considerable improvement in % metal ions sorption. This is due to at equilibrium stage the adsorption achieves its saturation, possibility no further adsorption occurs and the contact time has no longer effect on % sorption of metal ions.

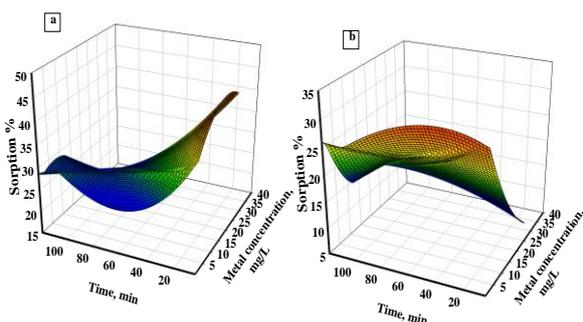


Fig. 7 : 3D plot the interaction effect of metal ions concentration (a) Ca (II) and (b) Mg (II) and contact time onto WCF.

3.3 Dyeing of WCF and WCF-Ca (II) with RY145:

Reactive dyes are widely used for the dyeing of cotton. These dyes are anionic in character and, in general, are water soluble due to the presence of sulphonic groups (SO_3^-) in the chemical structure. However, since cotton itself adopts an anionic surface charge in water, these dyes have low intrinsic affinity for the fibre. The repulsive charge between dye and cotton can be overcome by adding an electrolyte such as sodium chloride or sodium sulphate, which has the effect of screening the surface charge on the fibre. The large quantity of salt in the effluent, however, causes pollution of rivers and streams and upsets the biological equilibrium. In order to both reduce the usage of salt and increase in dye bath exhaustion, number of attempts have been made to modify the cotton fibre using compounds containing cationic groups [32].

The chemical modification of cotton in order to improve its dye ability with anionic dyes such as reactive, direct, acid, sulphur and vat dyes have received considerable attention in recent years. The advantages of this process include reduced environmental impact, and energy consumption. On the contrary, the treatment of cellulose fabric with metal ion before dyeing process proved to be more rapid, uniform, efficient, while also increasing the dye affinity and improving the fastness properties of

cotton fabric towards washing, light, rubbing and perspiration. It is considered a better alternative to the conventional dyeing technique due to the reduction of environmental impact, and energy consumption [33].

3.4 Dyeing kinetics :-

WCF-Ca (II) fabric were dyed with RY 145 and compared with the WCF. It is observed from figure 5 and table 1, that the E % and color strength K/S values respectively of WCF-Ca (II) are higher than those of the corresponding WCF. The higher E% and K/S values of WCF-Ca (II) indicate that the presence of metal ion (Ca (II)) on the surface of WCF which increases the dye affinity (from 57.89 % to 91.92 %), (from 14.29 to 19.56) respectively at 90°C towards the fabric. The negatively charged dye anions get attracted towards the fabric probably due to the polarity developed in the metal particles by induction which results in better bonding between the dye and fabric. The Ca (II) is small size can enter in between the polymer molecules and perhaps act as crosslinking agent which also contribute to the load sharing phenomenon during load application to the fabric [34].

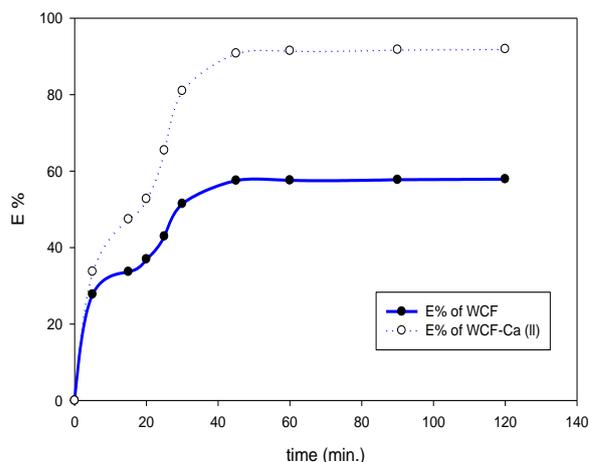


Fig. 8: Time-Exhaustion isotherms of RY 145 dye adsorption onto WCF and WCF-Ca (II) . [dyeing recipe: LR 1:50 , 10×10^{-3} g/l , 90°C].

Table 1 : Color strength K/S, L, a, b values of the WCF and WCF-Ca (II) using RY 145 at different temperature .

Sample	Temp. C	K/S	L*	a*	b*
WCF	50	6.45	70.59	22.80	53.39
WCF-Ca (II)	50	8.78	71.83	22.40	64.87
WCF	70	11.39	73.36	23.12	64.85
WCF-Ca (II)	70	14.83	74.93	22.90	65.72
WCF	90	14.29	74.73	23.45	66.23
WCF-Ca (II)	90	19.56	75.81	23.89	65.54

3.5 Adsorption isotherm

Adsorption isotherm models are widely used to describe and investigate mechanisms of adsorption. The equilibrium data was analyzed by the Langmuir and Freundlich isotherm model.

Langmuir adsorption isotherm

The Langmuir model describes monolayer sorption on distinct localized adsorption sites. It indicates no transmigration of the adsorbate in the plane of the surfaces and assumes uniform energies of monolayer sorption onto the sorbent surface [35].

The linear form of Langmuir equation can be written as follows:

$$C_e / q_e = 1/q_m K_L + C_e / q_m \quad (4)$$

where C_e (mgL^{-1}) is the concentration of metal ions Ca (II), Mg (II) and RY 145 at equilibrium, q_e (mgg^{-1}) is the amount of metal ions Ca (II), Mg (II) and RY 145 adsorbed by the WCF at equilibrium, q_{max} (mgg^{-1}) is the maximum adsorption capacity corresponding to monolayer coverage, and K_L (L/mg) is the Langmuir constant. The values of q_{max} and K_L can be calculated from plotting C_e / q_e versus C_e . The Langmuir plots for metal ions Ca (II), Mg (II) and RY 145 adsorption onto the WCF are obtained in figure (9,10) respectively. The values of the correlation coefficient R^2 for Langmuir plots more than 0.98 and from 0.96 to 0.98 for adsorption metal ions Ca (II) and Mg (II) and RY145 respectively into WCF. This suggests that the adsorption mechanism of metal ions Ca (II) and Mg (II) and RY 145 into WCF does follow the Langmuir model.

The calculated values of correlation coefficients predicted from this model, K_L and q_{max} for sorption of Ca (II) and Mg (II) and RY 145 onto WCF are represented in Table 2,3. Moreover, the data shows that the WCF significantly enhances the metal ions and RY145 adsorption (high Q_{max} & K_L) into WCF. Thus, the surface of WCF will take in metal ions and RY145 is due to polarity of WCF and its amorphous nature. WCF is highly negative in nature because the presence of groups (OH^-) along the polymer chain ability to bind with metal ions and dye, it is considered as an abio- way to subsequently increase the affinity between the metal ions, dye and the WCF rather than the conventional adsorption process.

The Freundlich isotherm is used to describe adsorption processes that occur on heterogeneous surfaces and active sites with different energies based on multilayer adsorption and equilibrium [36].

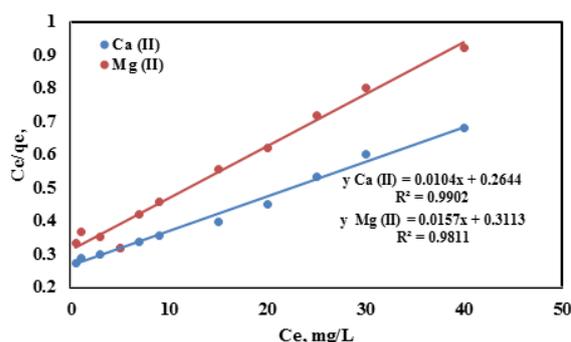


Fig. 9 : Langmuir adsorption isotherm of metal ions (Ca (II) and Mg (II)) into WCF.

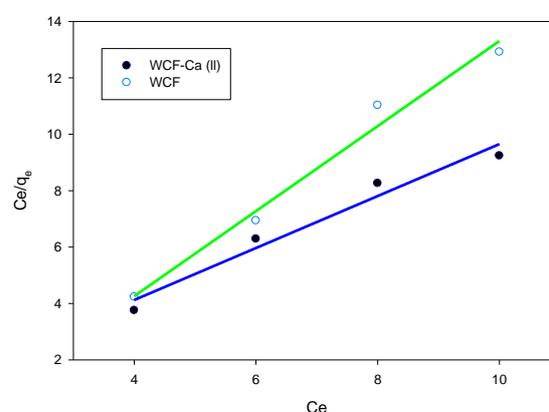


Fig. 10 : Langmuir adsorption isotherm of RY 145 into WCF and WCF-Ca (II) fabric . [dyeing recipe: LR 1:50 , 10×10^{-3} g/l , 90°C].

Freundlich adsorption isotherm

The linear form of Freundlich equation is given as:

$$\log q_e = \text{Log } K_F + 1/n \log C_e \quad (5)$$

where q_e is the metal ions Ca (II), Mg (II) and RY 145 concentration on the WCF at equilibrium, C_e (mgL^{-1}) is the concentration of metal ions Ca (II), Mg (II) and RY 145 in solution at equilibrium, and K_F ($\text{dm}^3 \text{g}^{-1}$) and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Freundlich constants are calculated from the slope and the intercept in figure 11,12 respectively, and are given in Table 2,3. The correlation coefficients R^2 less than 0.98 and 0.96 respectively for metal ions and RY 145 reflect that the experimental data do not agree with the Freundlich model. The values of $1/n$ (0.75 and 0.72) for metal ions Ca (II) and Mg (II) respectively, and (2.79 and 1.54) for WCF and WCF-Ca (II) respectively are more than 1, so it does not represent favorable adsorption conditions.

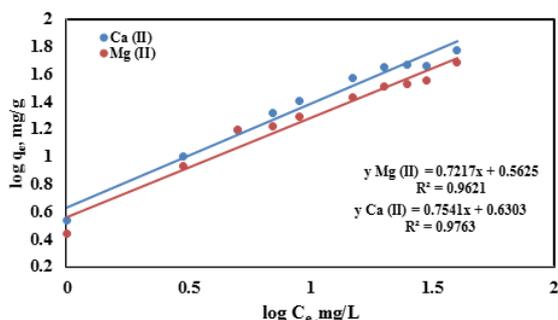


Fig. 11 : Freundlich adsorption isotherm of metal ions Ca (II) and Mg (II) into WCF.

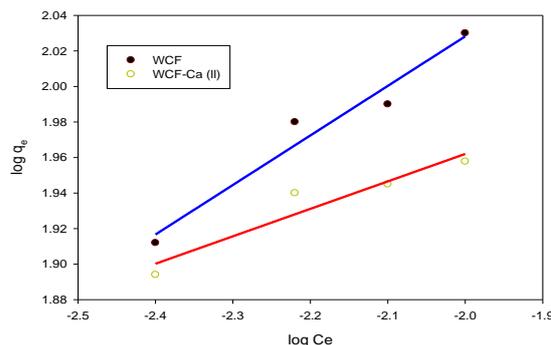


Fig. 12 : Freundlich adsorption isotherm of RY 145 into WCF and WCF-Ca (II) . [dyeing recipe: LR 1:50 , 10x10⁻³ g/l , 90^oC].

Table 2: Langmuir and Freundlich isotherm constants of adsorption of metal ions (Ca (II) and Mg (II)) into WCF.

Metal type	Langmuir adsorption isotherm				Freundlich adsorption isotherm		
	Q _{max} (mg/g)	k _L L mg ⁻¹	R _L	R ²	K _F (dm ³ g ⁻¹)	N	R ²
Mg (II)	63.69	0.05	0.338-0.976	0.9811	3.65	1.4	0.9621
Ca (II)	96.15	0.039	0.397-0.981	0.9902	4.27	1.3	0.9763

Table 3 : Langmuir, Freundlich isotherm constants of the dyeing process of RY 145 into onto WCF and WCF-Ca (II) fabric . [dyeing recipe: LR 1:50 , 10x10⁻³ g/l , 90^oC].

Fabric type	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q _{max} (mg g ⁻¹)	K _L x10 ² (dm ³ mg ⁻¹)	R ²	K _F dm ³ g ⁻¹	n/1	R ²
WCF	64.27	2.15	0.96	1.96	2.79	0.95
WCF-Ca (II)	92.17	2.37	0.98	2.82	1.54	0.91

3.6 Kinetics of adsorption

In order to examine the mechanism and rate-controlling step in the overall adsorption process, two kinetic models, pseudo-first-order, pseudo-second-order, are adopted to investigate the adsorption process.

Pseudo-First-Order kinetic model

It is the first equation for sorption of liquid/solid system and RY 145 based on solid capacity [37,38]. The Pseudo-first-order equation is written as follows: $\text{Log} (q_e - q_t) = \text{log } q_e - k_1 t / 2.303$ (6) where q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of pseudo first- order adsorption (min⁻¹). In order to obtain the rate constants of adsorption, the values of $\text{log} (q_e - q_t)$ were presented in Tables 4,5 . Where, k_1 is the rate constant of pseudo-first-order adsorption process (min⁻¹), q_e and q_t were the amount of adsorption capacity of metal ions and RY 145 adsorbed into WCF (mg/g) at equilibrium and at time t . The parameters k_1 and q_e could be calculated from the slope and intercept of

the straight line plots of $\text{log} (q_e - q_t)$ versus t were drawn in figure 13 for Ca (II) and Mg (II) at room temperature , figure 14, 15 for WCF and WCF-Ca (II) respectively . The correlation coefficients R^2 value is found to be unbeseeing for the present system R^2 less than 0.98 and 0.96 for sorption of metal ions and RY 145 respectively .This suggests that the pseudo-first-order kinetic model is not suitable to describe the adsorption process.

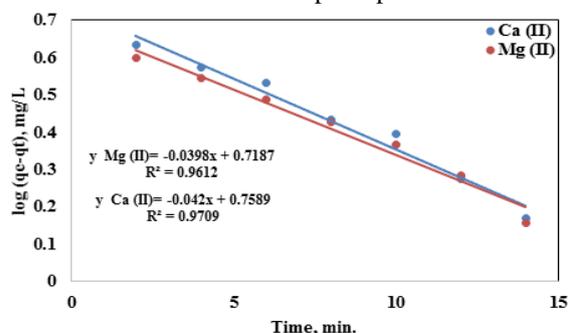


Figure (13): The pseudo first-order kinetic plots of metal ions Ca (II) and Mg (II) into WCF.

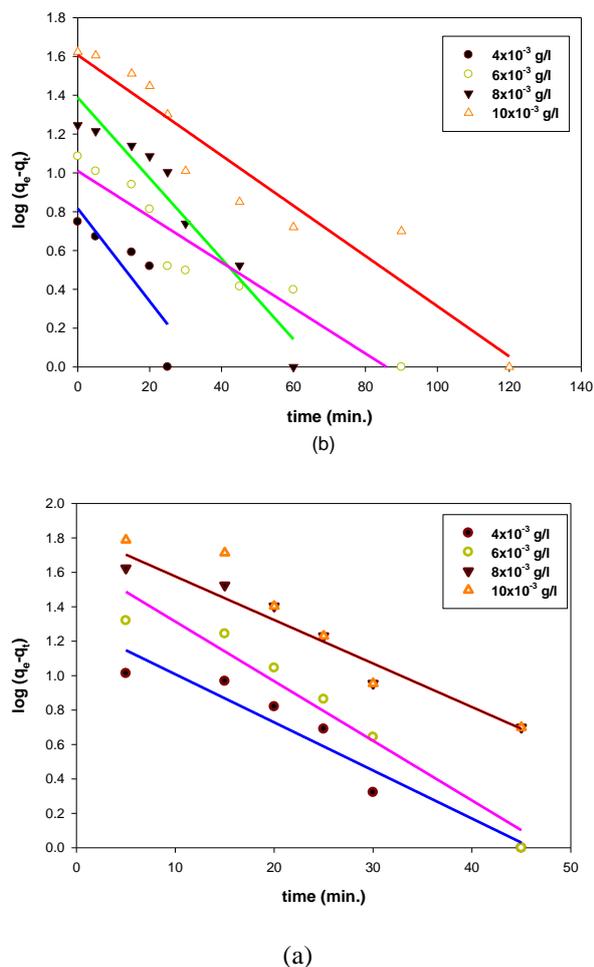


Fig. 14 : Kinetic plot for the adsorption of RY 145 into cotton fabric at 90 °C .

- Pseudo-first order of WCF.
- Pseudo-first order of WCF-Ca (II) .

Pseudo-Second-Order kinetic model

The pseudo-second-order kinetic model is another important model to investigate the kinetic of adsorption of dyes on textile fabrics [39,40]. The pseudo-second order kinetic model can be expressed in linear form as follows:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

Table 4 : Kinetic parameters for metal ions Ca (II) and Mg (II) into (WCF) as adsorbent.

Metal Type	Pseudo first-order model				Pseudo second-order model			
	k_1 (min ⁻¹)	q_e (Cal) mg/g	q_e (Cal) mg/g	R^2	K_2 (g/mg min)	q_e (Cal) mg/g	q_e (Exp.) mg/g	R^2
Mg (II)	0.0917	5.236	6.48	0.961	0.0256	6.803	6.48	0.983
Ca (II)	0.0967	5.741	9.48	0.971	0.0363	9.407	9.48	0.993

where k_2 is the rate constant of pseudo-second order adsorption (g/mg min). A plot of t/q_t versus t gives a linear relationship Figure 15,16 , from which q_e and k_2 were determined from the slope and intercept of the plot respectively and presented in Table 4,5 .

The correlation coefficients R^2 higher than 0.98 and 0.99 suggest that adsorption of metal ions and RY 145 respectively into WCF and WCF-Ca (II) predominantly follows the pseudo-second order kinetic model for the entire adsorption period, based on the assumption that the rate-limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate molecules [41].

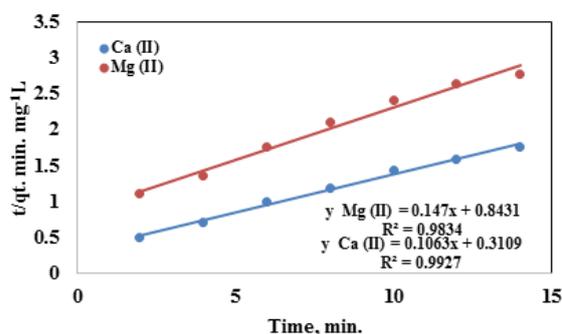


Figure (15):The pseudo second-order kinetic plots of metal ions (Ca (II) and Mg (II)) into WCF.

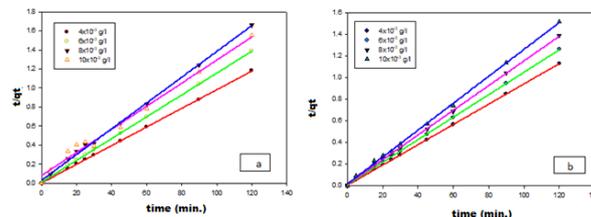


Fig. 16 : Kinetic plot for the adsorption of RY 145 into cotton fabric at 90 °C .

- Pseudo-second order of WCF.
- Pseudo-second order of WCF-Ca (II) .

Table 5 : Kinetic parameters of the dyeing process of RY 145 into WCF and WCF-Ca (II) at different concentrations .

Fabric Type	Conc. of dyeX10 ⁻³ (g/l)	Pseudo first-order model		Pseudo second- order model	
		$k_1 \times 10^2 (\text{min}^{-1})$	R ²	$K_2 \times 10^4$ (g/mg min)	R ²
WCF	4	2.71	0.70	0.95	0.99
	6	2.98	0.89	1.17	0.99
	8	4.78	0.93	1.74	0.99
	10	5.51	0.92	2.71	0.99
WCF-Ca (II)	4	5.82	0.91	1.41	0.99
	6	5.82	0.94	4.04	0.99
	8	6.43	0.94	5.71	0.99
	10	7.97	0.94	11.95	0.99

3.7 Determination of WCF and WCF- Ca (II) properties :-

Color fastness properties

The effect of Ca (II) treatment on physical properties has been studied. The dye and Ca (II) should have penetrated into the WCF, but stay mostly on the internal side of the surface since dyed fabrics possess very good crocking fastness. The data are collected in table 6 .It is inferred from the data that there is a maximum light and washing grade fastness values exhibit excellent rates at 5 which achieved the requirements for industrial use for WCF-Ca (II) fabric as compared to the WCF. This may be attributed to the strong attachment of the Ca (II) with WCF active sites through its whole structure. The lower fastness grade properties of

WCF with might be due to the unwell- adhering dye particles onto fabric. Higher grade values mean lower dye content in waste water as previously explained.

With respect to perspiration data, the results in tables 6 also indicate very good to excellent color fastness grade for WCF-Ca (II) and poor for WCF towards both acidic and alkaline perspiration. The perspiration data of WCF-Ca (II) sample assest the important requirement for comfort properties which consider as a base of the fundamental requirements of medical fabrics. In general the results give very good indication for enhancement the functionality of WCF with Ca (II) that became a smart treatment applied as a novel approach to textile dyeing and finishing [42,43].

Table 6 : Fastness properties of WCF and WCF-Ca (II) fabric in presences of various temperatures .

Temp. °C	WCF				WCF-Ca (II)			
	Washin g	Light	Perspiration		Washin g	Ligh t	Perspiration	
			Acid	Alkali			Acid	Alka li
50	3-4	3-4	3-4	3-4	4	4-5	4-5	4-5
60	3-4	3-4	3-4	3-4	4	4-5	4-5	4-5
70	4	3-4	3-4	3-4	4	4-5	4-5	4-5
80	4	4	4	4	4-5	5	4-5	5
90	4	4	4	4	4-5	5	5-6	5-6

4. Conclusion:

In this study, the biosorbent (WCF) was characterized by SEM and FTIR . The conditions were optimized and adsorption-desorption experiments were carried out accordingly. Adsorption process of metal ions on the WCF could well conform with the Langmuir model and adsorption capacity of raw cotton was 42 mg g⁻¹ for Ca(II) and 35 mg g⁻¹ for Mg(II). Adsorption-desorption experiments revealed that WCF was a promising material for the removal of toxic metal from the polluted water. Moreover, the WCF is not only

inexpensive and convenient, but also can be easily recycled, especially suitable for the treatment of sudden pollution in the river. then WCF after adsorption process (WCF-Ca (II)) is used in dyeing with RY 145 for environmental benefits . The higher E% and K/S values of WCF-Ca (II) indicate that the presence of metal ion on the surface of WCF which increases the dye affinity . The overall fastness properties to light, perspiration, washing for the colored samples are ranging from very good to excellent.

Conflicts of interest

“There are no conflicts to declare”.

Formatting of funding sources

No funding sources

5. References :-

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