

SYNTHESIS AND USE OF MODIFIED WOOL FIBERS LOADED WITH METAL IONS FOR THE ADSORPTION OF ANIONIC DYES FROM AQUEOUS SOLUTIONSAMEL EL GHALI^{A,*}, SAFA HALLOUL^B, MOHAMED HASSEN V BAOUAB^A^A MICROELECTRONICS & INSTRUMENTATION LABORATORY, F.S.M. UNIVERSITY OF MONASTIR, TUNISIA.^B NATIONAL ENGINEERING SCHOOL OF MONASTIR, UNIVERSITY OF MONASTIR, TUNISIA.**ABSTRACT**

In this work, new wool-grafted-thiol (wool-g-t) chelating support was synthesized using sodium thiocyanate. The modified fibers were then loaded with Cu(II), Co(II) and Fe(III). The investigations into structural changes, which occurred during the modification of wool fibers followed by its binding to the metal ions, were performed using FTIR Spectroscopy analysis. Afterwards, batch adsorption tests were carried out with native wool (NW), wool-grafted-thiol (wool-g-t) chelating fibers and metal-wool-grafted-thiol (metal-wool-g-t) fibers in order to evaluate the adsorption efficiency of each adsorbent for the removal of AY 17 from aqueous solutions. The effects of temperature and type of adsorbent on dye uptake were investigated. Results were analyzed by Langmuir, Freundlich and Jossens equations at different temperatures. The Jossens model was found to be in better correlation with the experimental data. The thermodynamic parameters were also calculated from the adsorption equilibrium measurements.

KEYWORDS

Wool fibers, thiol groups, adsorption, modelling, thermodynamic parameters

1. INTRODUCTION

Wastewater effluents from different industries, such as textile industry, contain several varieties of synthetic dye stuffs which are difficult to biodegrade due to their complex aromatic structures that give them physico-chemical, thermal and optical stability. (Han et al., 2008) Therefore, the removal of such agents from aqueous effluents became a significant environmental challenge. Various technologies have been developed to remove dyes from Wastewater over the years. The most important of these technologies included biodegradation (Mayur et al., 2017), photodegradation (Liu et al., 2013), coagulation/flocculation (Yeap et al., 2014) and adsorption (Ghaedi et al., 2012; El Qada et al., 2008). Among these measures, adsorption is considered as a powerful and favorable technique due to its simplicity of operation, sludge free and wide application range (Yao et al., 2015). Adsorption with activated carbon is an important and an efficient method to clean up effluents and wastewater. In spite of its prolific use, the activated carbon has some limits such as its high cost, the need of its regeneration after exhausting and the loss of its adsorption efficiency after regeneration. These problems have led many workers to search for the use of new, cheap and indigenous alternative materials obtainable from natural resources for the removal of dyes from aqueous solutions (Derrouiche et al., 2015; Şener, 2008; Fiorentin et al., 2010). Meantime, many modification methods have been invented to enhance the adsorption capacities of these natural by-products (El Ghali et al., 2011).

In recent years, the adsorption capacity of natural protein fibers has been explored for the production of new kinds of adsorbents (Zheljazkov et al., 2009). Wool keratin fibers are one of the most popular natural biopolymer and they are usually used for high-grade textiles due to their various specific properties such as elasticity handle, warmth retention and fullness (Yuan et al., 2010; Jiugang et al., 2012; Wan and Yu, 2011).

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As protein fiber, wool consists of polar and ionisable groups on the side chain of amino acid residues able to bind other charged organic and inorganic molecules (Taddei et al., 2003). In this context, wool has been used as an adsorbent to remove heavy metal pollutants from industrial effluents and to purify contaminated water supplies (Zheljazkov et al., 2009).

The metal uptake by wool fibres can be improved by chemical modification with suitable chelating agents able to coordinate metal ions (Taddei et al., 2003; Freddi et al., 2001). The incorporation of metal ions into wool fibers could confer to this material new performances such as the enhancement of its dye adsorption capacity which is the aim of the present work. Therefore, in this investigation, natural wool fibers were modified by grafting thiol groups in the attempt to prepare chelating material that possesses strong affinities toward metal ions. The potential of modified wool fibers loaded with metal species and unloaded supports was evaluated for the adsorption of AY 17 from aqueous solutions under batch conditions. Equilibrium data are attempted by three adsorption isotherms namely Langmuir, Freundlich and Jossens isotherms in order to select an appropriate isotherm model that describes the observed sorption phenomena of the selected dye onto the prepared supports. Thermodynamics parameters of the adsorption were also investigated and reported.

2. EXPERIMENTAL

2.1. Materials and methods

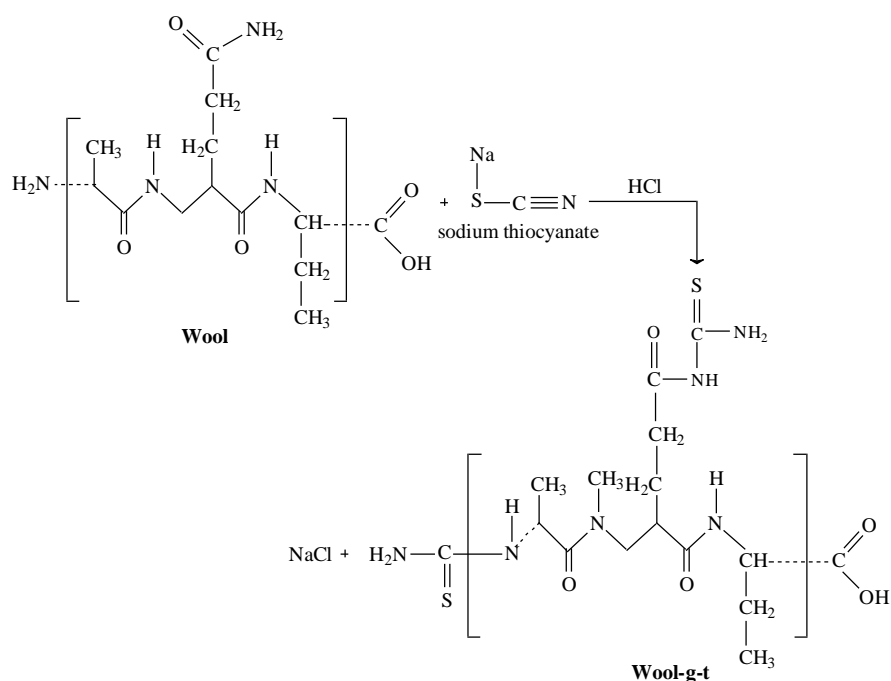
Wool fibers, employed in all experimental work, were procured commercially. Before being used, the fibers were bleached with a solution containing 25 mL.L⁻¹ hydrogen peroxide (110 vol.) and 1 mL.L⁻¹ ammonia (30%) at 55 °C for 60 min, keeping the material to liquor ratio at 40:1. Therefore, the bleached material was neutralized with formic acid solution then thoroughly washed with distilled water and finally dried at 40 °C still constant weight. All reagents [sodium thiocyanate, formaldehyde, HCl, Copper sulfate (CuSO₄), ferric chloride (FeCl₃) and Cobalt Chloride (CoCl₂) were purchased from Sigma-Aldrich Company and used without further purification. The Acid Yellow 17 (AY 17) used in the adsorption experiments was also supplied by Sigma-Aldrich Company and was employed in its technical grade. The chemical structure and characteristics of the selected dye are given in Table 1.

Table 1: Chemical and physical characteristics of AY 17

Color Index Number	λ_{\max} (nm)	Molecular weight (g.mol ⁻¹)	Formula
18965	401	551.29	

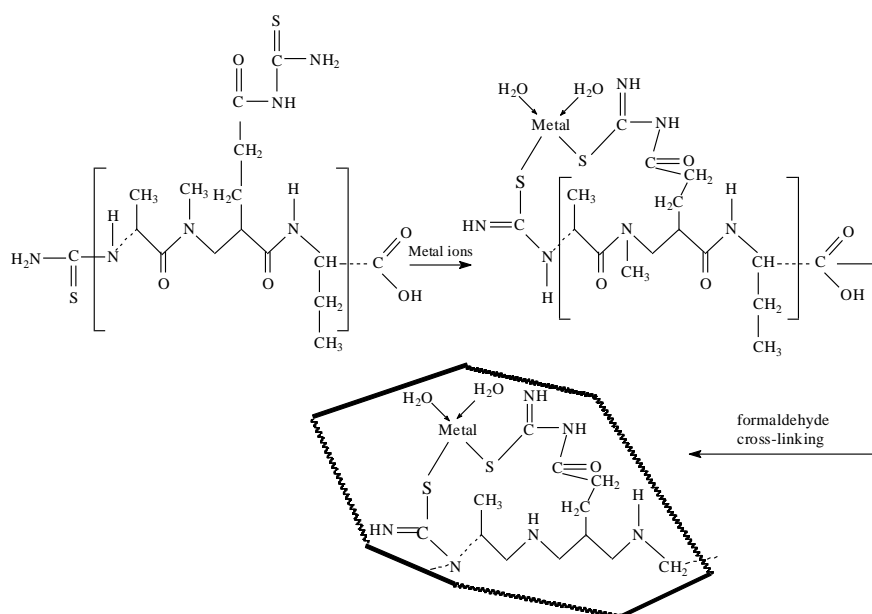
2.2. Preparation of metal/wool-g-t-chelating fibers

The wool-g-t support was synthesized in one step as can be seen in Scheme 1.



Scheme 1: Synthesis of wool-g-t chelating fibers

It was prepared according to the following stepwise procedure. 1 g of the pretreated wool fibers was immersed in 200 mL 5% (w/v) of sodium thiocyanate aqueous solution. 4 mL of HCl (0.5M) solution were added and the mixture was refluxed for 2 h at 80 °C. The obtained product was then collected, rinsed with distilled water and finally dried under vacuum at 40 °C for 72 h. The obtained wool-g-t chelating fibers were then loaded with metal ions by soaking 1g of the fibers in a glass bottle containing 200 mL of a metal solution at pH = 5. The concentration of metal ions used to saturate the adsorbent was 10 g.L⁻¹. The suspension was stirred at room temperature for 2h. The metal ion-imprinting route was then carried out by soaking the dried metal/wool-g-t fibers in 100 mL of formaldehyde solution (30%). The mixture was refluxed for 2h at 80 °C after adjusting the pH to 5 using diluted HCl solution. The resulting support was then dried at 40 °C under vacuum for 72 h. The formaldehyde solution was used in order to: (1) stabilize the metal in its novel matrix, (2) avoid the metal desorption from the fibers and (3) evade the precipitation of the selected dye if the (metal/dye) complex is more stable than the complex (metal/fibers). The metal ion imprinting process was presented in Scheme 2.



Scheme 2: Ion-imprinting of metal ions in wool-g-t fibers

2.3. Characterization of the modified materials

2.3.1. Evidence of grafting

The percentage grafting $G(\%)$ was calculated from the weight uptake, applying the following equation:

$$G(\%) = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

Where W_0 and W are the weights of the wool fibers before and after the graft of thiol groups, respectively.

2.3.2. Fourier transform-infrared spectroscopy

The FTIR spectra were obtained from KBr pellets using a Fourier Transform Infrared Spectrometer (Nicolet® 510M) operating in transmission mode in the range of 500-4000 cm^{-1} .

2.4. Adsorption of AY 17 onto prepared adsorbents

The sorption of AY 17 on native wool fibers (NW), wool-grafted-thiol (wool-g-t) chelating fibers and metal ion-imprinted grafted wool fibers [(Cu(II)/wool-g-t), (Co(II)/wool-g-t), and [Fe(III)/wool-g-t)] were carried out using a batch process. Batch experiments were performed by agitating a known amount of adsorbent (0.1 g) placed in contact with 100 mL of dye aqueous solution using an Ahiba Nuance® laboratory machine. Adsorption tests were evaluated at $\text{pH} = 7$ by varying temperature between 20 and 80 °C for a period of 2 h. It has been verified initially that this time was sufficient to equilibrate the heterogeneous system formed. Each adsorbent was finally removed by filtration through 0.45 μm membrane. The filtrate was then analyzed for residual dye concentration by analytical method using a JANWAY® 6100 spectrophotometer at 401 nm. The dye concentration retained in the adsorbent phase was calculated using the following relationship:

$$Y_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

Where C_0 and C_e (mg.L^{-1}) are the initial and the equilibrium dye solution concentrations, respectively, V (L) is the volume of the solution, and W (g) is the weight of the adsorbent.

3. RESULTS AND DISCUSSIONS

3.1. Evidence of grafting

Results revealed that the degree of grafting of thiol groups onto wool material was equal to 3%. The obtained value could be attributed to the fact that the grafting of these chemical functions is only carried out onto the terminal NH_2 groups of the wool fibers.

3.2. Fourier transform-infrared spectroscopy (FTIR)

The successive steps of the metal/wool-grafted-thiol fibers synthesis were detected using FTIR spectra, and the results were displayed in Figure 1. The spectra of the native wool fibers (Figure (1a)) showed a broad band in the range of 3152-3500 cm^{-1} which may be attributed to the -NH-stretching and -SH bonds. The peaks at 1633, 1533, and 1231 cm^{-1} belonging to -CONH- (amide I, amide II and C-N stretching of amide III, respectively) (Monier et al., 2010). After sodium thiocyanate treatment, the characteristic band of NH_2 groups observed in native wool fibers spectra (Figure (1a)) was reduced in the grafted wool fibers spectra (Figure (1b)). This could be explained by the reaction between these functional groups and the NaSCN. The sharp peak given at 1236 cm^{-1} (Figure (1b)) could be assigned to the C=S groups. The metal/wool-g-t spectrum (Figure (1c)) revealed the disappearance of the peak corresponding to C=S groups. This confirmed that the metal ions were successfully chelated in the wool-g-t support. After the formaldehyde cross-linking (Figure (1d)), the IR spectrum of metal/wool-g-t ion-imprinted fibers exhibited the appearance of a new band situated between 2992 cm^{-1} and 2885 cm^{-1} that could be attributed to the aldehyde group (- CH_2 -).

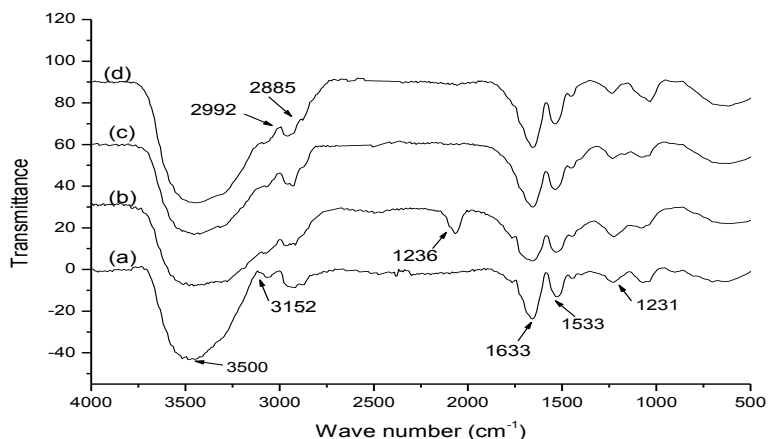


Figure 1: FTIR spectra of: (a) NW, (b) wool-g-t, (c) [metal/wool-g-t] and (d) metal/wool-g-t ion-imprinted fibers

3.3. Adsorption of AY 17 onto prepared supports

3.3.1. Effect of adsorbent type

The dye uptake removal capacity can be assessed using the adsorption isothermal experiments. In this section, we have evaluated the adsorption equilibrium of AY 17 on native wool fibers [NW], wool-grafted-thiol fibers [wool-g-t] and metal/wool-grafted-thiol complex [Cu(II)/wool-g-t, Co(II)/wool-g-t and Fe(III)/wool-g-t] at 20 °C. Figure 2 shows curves of Y_e vs. C_e for the adsorption of AY 17 onto the five tested supports.

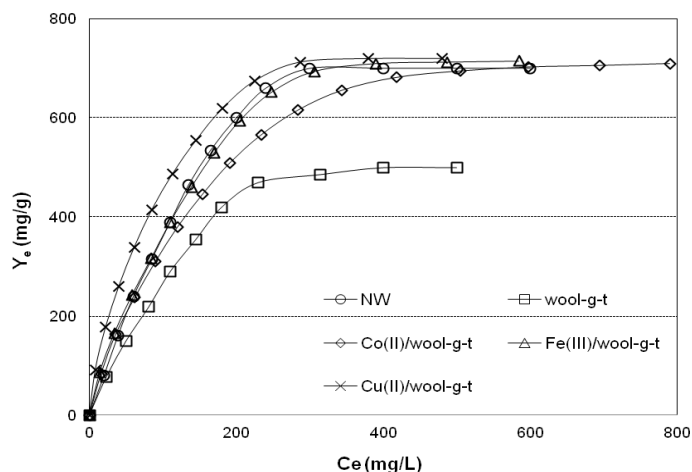


Figure 2: Adsorption isotherms of NW, wool-g-t and [metal/wool-g-t] at 20°C.

A limit value Y_{ref} ($\text{mg}\cdot\text{g}^{-1}$) is observed for the selected dye and high adsorption capacities are found: AY 17 being adsorbed to a capacity of 720, 715, 710, 700 and 500 mg (dye)/g [Cu(II)/wool-g-t], [Fe(III)/wool-g-t], [Co(II)/wool-g-t], (NW), and (wool-g-t) fibers, respectively.

Figure 3 summarizes possible interaction mechanisms between AY 17 and the different used adsorbents.

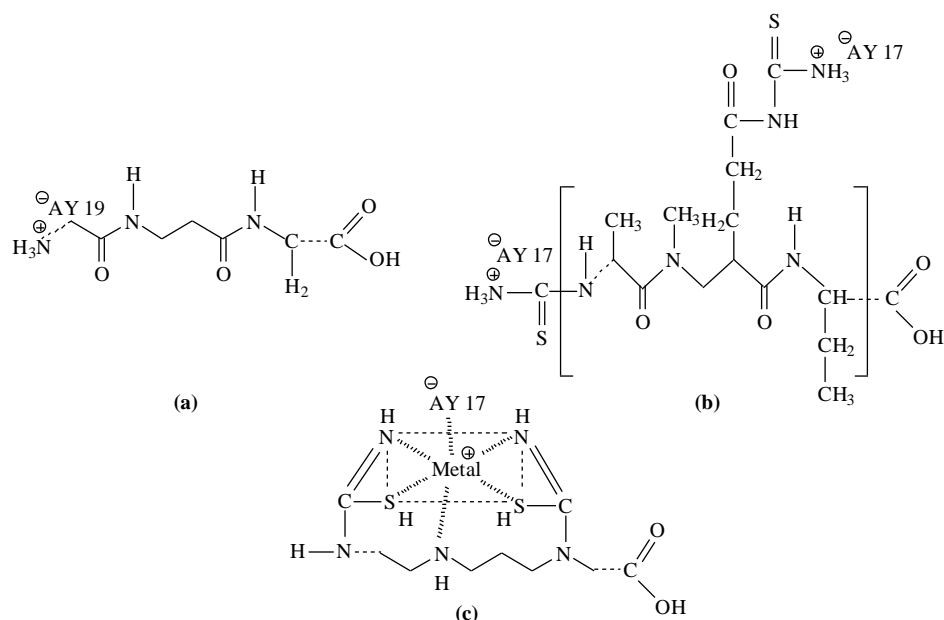


Figure 3: Proposal of interaction modes between AY 17 and (a) NW fibers, (b) wool-g-t fibers and (c) [metal/wool-g-t] complex.

The obtained results revealed that the adsorption effectiveness depended on the nature of the used substrate. Indeed, the amount of adsorbed selected dye was improved using the grafted wool fibers followed by the loading of metal ions onto the modified supports. This revealed that AY 17 can act as an efficient ligand for coordinating metal already involved in grafted wool fibers. In addition, the wool-g-t support exhibited the lowest adsorption capacity compared to the NW and the Metal/wool-g-t ones. This could be explained as follows. In the case of NW, the dye is adsorbed on the positive charge of the ammonium function of this support. For the Metal/wool-g-t, the same dye is adsorbed on the coordinated metal of this complex. Whereas, in the case of wool-g-t substrate, the positive charge is engaged in mesomerism which destabilizes it and reduces its reactivity. Furthermore, the adsorption capacities of [Cu(II)/wool-g-t], [Fe(III)/wool-g-t], [Co(II)/wool-g-t] supports are very close and are within the limits of error measurement of concentrations. This suggested that the adsorption is not largely depended on the type of metal and it is due to coulomb interactions.

3.3.2. Effect of temperature

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. Therefore, the effect of temperature on AY 17 adsorption by NW, wool-g-t and [metal- wool-g-t] supports was investigated in the range of 20-80°C. For NW fibers (Figure 4), the AY 17 adsorption was not found to be influenced by change in temperature from 20-80 °C.

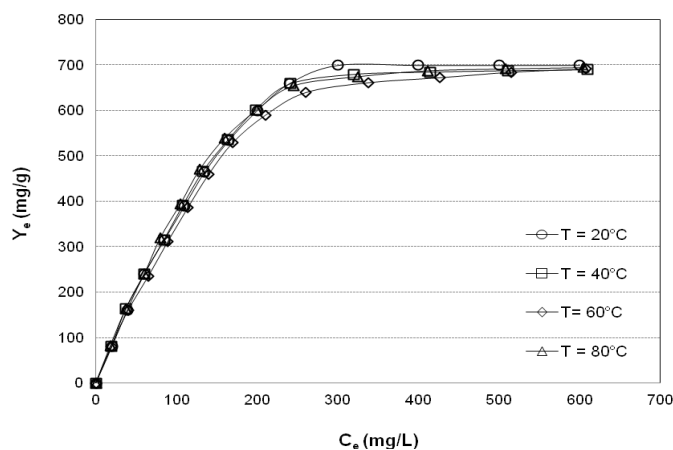


Figure 4: Effect of temperature on the adsorption of AY 17 onto NW support.

The obtained result could be due to the wealth of the fiber's surface in adsorbent functions which might exhibit various types of interactions via the tested dye. Indeed, each function has its own thermodynamic properties. Consequently, if the adsorption on one of the function is endothermic and on another one is exothermic, the energy assessment will be athermic as can be explained by Figure 5.

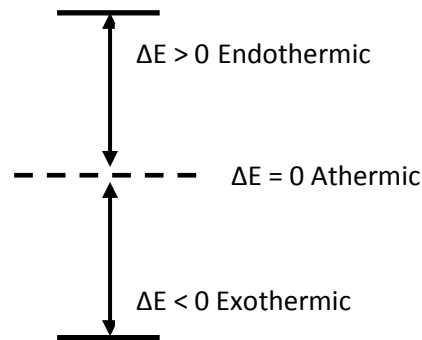


Figure 5: Proposal of energy assessment of adsorption phenomenon of AY 17 onto NW support

The adsorption of the selected dye by wool-g-t fibers is given in figure 6.

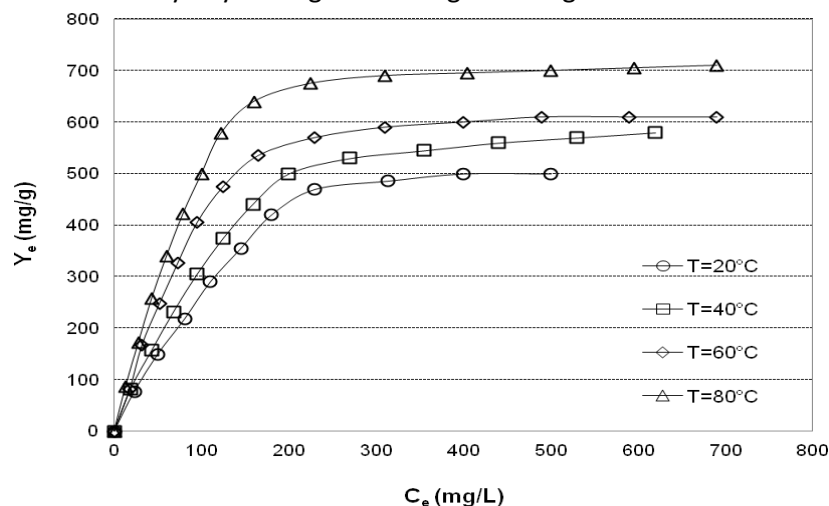


Figure 6: Effect of temperature on the adsorption of AY 17 onto wool-g-t support

As can be seen, the removal of dye increased with increase in temperature indicating that a high temperature favored AY 17 uptake by adsorption onto chemically modified wool fibers. The augmentation in adsorption with rise in temperature could be attributed to: (1) the increase in the number of active surface sites available for adsorption, (2) the increase in the porosity and in the pore volume of the adsorbent, (3) the increase of the diffusion rate of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle due to decrease in the viscosity of the solution and (4) the increase in the mobility of the dye molecules with an increase in their kinetic energy (Chowdhury et al., 2011). The increase of the equilibrium uptake with increase in temperature means that the dye adsorption is controlled by an endothermic process.

For the [metal/wool-g-t] complex, we have depicted the adsorption of the selected dye using [Cu(II)/wool-g-t] support (Figure 7). The other adsorbents, namely [Co(II)/wool-g-t] and [Fe(III)/wool-g-t] presented the same adsorption behavior than that of [Cu(II)/wool-g-t] complex (Figures are not shown). As seen from Figure 7, the adsorption capacity of the selected dye decreased with increasing temperature. The obtained results could be explained by the weakening of the sorptive forces between the active sites on the adsorbent and the dye molecules, and also between adjacent dye molecules on the adsorbed phase (Ofomaja and Ho, 2007). In addition, with the increase of temperature, the solubility of the tested dye increased. Thus, the interaction forces between the solute and the solvent were stronger than those between solute and adsorbent. Consequently, the solute became more difficult to be adsorbed (Crini and

Badot, 2008). The observed trend in decreased dye uptake capacity with the enhancement of temperature implied that the adsorption of AY 17 by [metal/wool-g-t] complexes is mainly controlled by an exothermic process. The above results will be further substantiated by the various thermodynamic parameters evaluated for the adsorption phenomenon.

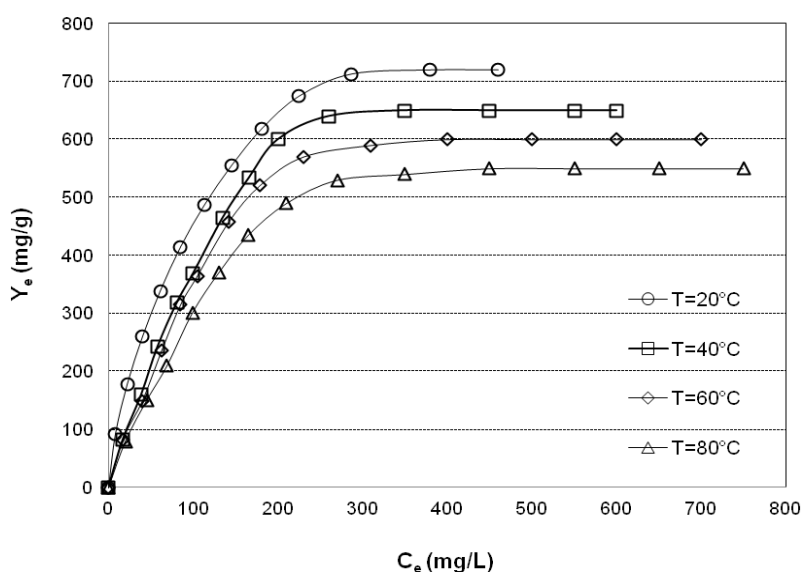


Figure 7: Effect of temperature on the adsorption of AY 17 onto Cu(II)/wool-g-t support

3.4. Adsorption isotherms

The adsorption equilibrium isotherm data is valuable in describing the distribution of adsorbate molecules with the liquid and the solid phases when the adsorption process reaches equilibrium. The adsorption prediction of the extent of adsorption needs the correlation of equilibrium data with theoretical equations. Therefore, to optimize the design of an adsorption system for removing AY 17 from solutions, it is essential to establish the most appropriate correlation for the equilibrium curves. In this study, the relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by three isotherm models namely Langmuir, Freundlich and Jossens.

3.4. 1. Langmuir model

The Langmuir adsorption model can predict monolayer coverage of the adsorbate on the outer surface of the adsorbent. Additional hypothesis is that adsorption occurs at specific homogeneous sites within the adsorbent and there is no migration or interaction between the sorbed molecules (Doulati et al., 2008). Furthermore, the sorption of each sorbate molecule onto the surface has equal sorption activation energy (Wang and Li, 2005). The expression of the Langmuir isotherm equation is represented by the following linear form:

$$\frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (3)$$

Where C_e (mg.L^{-1}) is the equilibrium concentration of the adsorbate, Y_e (mg.g^{-1}) is the amount of adsorbate adsorbed per unit mass at equilibrium, Q (mg.g^{-1}) denotes the theoretical maximum monolayer adsorption capacity of the adsorbent and b (L.mg^{-1}) is the Langmuir constant related to the affinity of binding sites. The Langmuir constants Q and b were determined from the slope and the intercept of the plot and are presented in Table 2.

Table 2: Langmuir Constants and Thermodynamic Parameters for Adsorption of AY 17 onto NW, wool-g-t and [metal/wool-g-t] adsorbents

Adsorbent	T (°C)	Y_{ref} (mg.g ⁻¹)	Q (mg.g ⁻¹)	b (L.mg ⁻¹)	R_L	R^2	ΔG° (kJ.mol ⁻¹)	ΔS° (J.K ⁻¹ .mol ⁻¹)	ΔH° (kJ.mol ⁻¹)
Cu(II)/ wool-g-t	20	720	909.09	0.0114	0.108	0.993	-5.7034	-16.9	-10.572
	40	650	833.33	0.0087	0.149	0.986	-5.1613		
	60	600	909.09	0.006	0.206	0.985	-4.8717		
	80	550	769.23	0.0063	0.221	0.972	-4.6710		
Fe(III)/ wool-g-t	20	715	909.09	0.0072	0.161	0.983	-4.5987	-16.7	-9.6159
	40	600	769.23	0.0072	0.186	0.980	-4.4827		
	60	500	666.66	0.0067	0.229	0.980	-4.1544		
	80	400	526.31	0.0064	0.279	0.988	-3.5917		
Co(II)/ wool-g-t	20	710	833.33	0.0073	0.160	0.990	-4.4055	-61.7	-22.759
	40	450	555.55	0.0070	0.238	0.993	-3.5235		
	60	410	526.31	0.0054	0.309	0.988	-2.8726		
	80	250	384.61	0.0024	0.619	0.974	-0.5085		
wool-g-t	20	500	696.37	0.0070	0,238	0.974	-3.6369	54.6	12.44
	40	580	763.58	0.0074	0,239	0.983	-4.4023		
	60	610	763.37	0.0117	0,156	0.964	-5.8793		
	80	710	943.49	0.0100	0,193	0.972	-6.7812		
NW	20	700	1409	0.0035	0,545	0.996	-3.7342	17.9	1.53
	40	690	1297.03	0.0040	0,485	0.994	-4.1315		
	60	692	1406.14	0.0033	0,505	0.997	-4.1831		
	80	695	1186	0.0048	0,419	0.994	-4.9081		

As seen from Table 2, the experimental data exhibited relatively good correlation coefficients ($0,964 < R_2 < 0,997$), indicating the acceptability of the Langmuir model for the adsorption of AY 17 in all cases. The obtained results also revealed that the calculated values of Q, estimated from the Langmuir model, are lower than the experimental ones (Y_{ref}), suggesting that the adsorptive functional groups of the used adsorbents were not completely used during the ongoing adsorption process.

The values of b (Table 2) showed different trend from one adsorbent to another by varying temperature. Indeed, for NW fibers, b values were not significantly influenced by the change of temperature. In the case of wool-g-t fibers, b constants exhibited significant increment with the rise in temperature, indicating that the enhancement of this parameter induced a higher maximum adsorption capacity. This is an indication of

the endothermic nature of the process as was earlier shown. For the metal/wool-g-t complexes, the values of b decreased with increase in temperature, which accounts for the exothermic nature of the adsorption process.

In general, good adsorbents have a high b value (Areco and Afonso, 2010). In the present study, [Cu(II)/wool-g-t] complex satisfied this supposition. In addition, a large value of b obtained at 20°C implied strong bonding of AY 17 to the [metal/wool-g-t] complexes at lower temperatures (Feng et al., 2009). The opposite trend was observed in the case of wool-g-t fibers. Indeed, the bonding between the selected dye and this adsorbent became strong at higher temperatures (Anirudhan and Rejeena, 2013).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation:

$$R_L = \frac{1}{1 + b \times C_{ref}} \quad (4)$$

Where C_{ref} (mg.L^{-1}) is the highest fluid-phase concentration.

The magnitude of this parameter gives information about the favorability of adsorption process. The calculated values of separation factor for the tested adsorbents at different temperatures are presented in Table 3. As can be seen, the values of R_L are all in the range 0-1, indicating the suitability of AY 17 adsorption process at all the experimental temperatures. By comparing the results of the values of R_L for the different adsorbate/adsorbent systems, it can be concluded that the adsorption of AY 17 is more favorable by using the [Cu(II)/wool-g-t] complex (Anirudhan and Rejeena, 2013).

By using the data obtained from adsorption isotherms, thermodynamic parameters such as Gibbs free energy change (ΔG°), change in entropy (ΔS°) and $^\circ$) change in enthalpy (ΔH°) at different temperatures were evaluated using the following equations:

$$\Delta G^\circ = -RT \cdot \ln K_L \quad (5)$$

$$K_L = Q \cdot b \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (7)$$

Where R ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$) is the gas constant, T (K) is the solution temperature in Kelvin and K_L is Langmuir equilibrium constant. The plot of ΔG° versus T yields a straight line from which ΔS° and ΔH° were calculated from the slope and intercept, respectively. The results are listed in Table 2.

The negative values of ΔG° in all cases suggested the feasibility and the spontaneous nature of the adsorption processes. In addition, the increase in the absolute value of ΔG° with increasing temperature indicated that higher temperatures facilitated the uptake of AY 17 by wool-g-t adsorbent (Kul and Koyuncu, 2010). The opposite trend was obtained in the case of [metal/wool-g-t] complexes. Indeed, the decline in negative values with rise in temperature showed an increase in the achievability of adsorption at lower temperatures as proved in the previous section (Kul and Koyuncu, 2010).

The positive values of ΔH° for the adsorption of AY 17 onto wool-g-t fibers indicated the endothermic nature of the adsorption reaction of the selected dye. This suggested that a large amount of heat is consumed to transfer AY 17 molecules from aqueous into both solid phases (Kul and Koyuncu, 2010). Opposite behavior was found in the case of [metal/wool-g-t] complexes. Indeed, the negative value of change in enthalpy indicated the exothermic nature of dye sorption, favored with the temperature decrease.

As can be seen from Table 2, the change entropy ΔS° results varied from one adsorbent to another. In fact, the obtained positive ΔS° values corresponded to an increase in the degrees of freedom of the solid-liquid interface during adsorption of AY 17 onto native and grafted wool fibers (Chen et al., 2010). This can be

explained as follows. The positive ΔS° value took place as a result of redistribution of energy between the adsorbate and the adsorbent. Indeed, before adsorption occurs, the dye molecules near the surface of the adsorbent will be more ordered than in the following adsorbed state and the ratio of free solute molecules interacting with the adsorbent will be higher than in the adsorbed state. Consequently, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS° and randomness will increase at the solid–solution interface during the process of adsorption (Kul and Koyuncu, 2010).

However, in the case of [metal/wool-g-t] adsorbents, values of ΔS° were negative corresponding to a decrease in the degree of freedom of the adsorbed species. This also suggested the probability of favorable sorption with no structural change at solid-liquid interface (Akhtar et al., 2007).

In addition, the obtained results revealed that AY 17 dye molecules in aqueous solution are in much more disordered distribution than they are in adsorbed state which displayed the strong affinity of this dye towards [metal- wool-g-t] complexes (Susmita and Bhattacharyya, 2008).

3.4.2. Freundlich model

The Freundlich isotherm is an empirical model that describes heterogeneous adsorptive energies on the adsorbent surface and is expressed as follows:

$$\ln Y_e = \ln P + \frac{1}{n} \ln C_e \quad (8)$$

Where P ($L \cdot g^{-1}$) is a Freundlich constant related to adsorption capacity of the adsorbent, $1/n$ is the adsorption intensity, which gives an indication of the favorability of adsorption. The constants P and n of the above model could be determined from the intercept and the slope of Equation 8. The calculated parameters and the corresponding correlation factors R^2 are given in Table 3.

Results exhibited low correlation coefficients ($0.877 < R^2 < 0.966$), indicating that the Freundlich model was not sufficiently for explaining the relationship between the amount of sorbed AY 17 and its equilibrium concentration in the solution.

From Table 3, it is apparent that values of the Freundlich constant, $1/n$ obtained for the present systems indicated favorable adsorption, as it lies between 0 and 1 (Feng et al., 2009). Also, a higher value of n indicated better adsorption and formation of relatively strong bond between the adsorbate and the adsorbent (Kul and Koyuncu, 2010).

The Freundlich parameter P is useful in the evaluation of the adsorption capacity of the tested adsorbents. As seen from Table 3, values of P increased with the increment of temperature for the uptake of the dye by the wool-g-t support. This indicated that the adsorption capacity of this adsorbent increased with increasing of this parameter, confirming the endothermic adsorption behavior. This is consistent with the effect of the temperature on AY 17 adsorption (Chen et al., 2010).

In the case of [metal/ wool-g-t] complexes, the highest P value was observed at 20 °C confirming that the loading capacities of the studied adsorbents decreased with the rise in temperature (Chakraborty et al., 2011).

Moreover, in all studied temperatures, the P values of [Cu(II)/ wool-g-t] complex are much higher than that for [Co(II)/ wool-g-t] and [Fe(III)/ wool-g-t] complexes. This showed the superiority of this material in the adsorption of AY 17 from aqueous solutions.

Table 3: Freundlich Constants for Adsorption of AY 17 onto NW, wool-g-t and [metal/wool-g-t] adsorbents

Adsorbent	T (°C)	P	n	R ²
Cu(II)/wool-g-t	20	66.008	2.435	0.957
	40	48.212	2.234	0.940
	60	35.656	2.031	0.944
	80	32.030	2.057	0.945
Fe(III)/wool-g-t	20	50.220	2.278	0.937
	40	47.047	2.384	0.925
	60	38.647	2.379	0.932
	80	28.800	2.332	0.951
Co(II)/wool-g-t	20	58.669	2.544	0.936
	40	39.328	2.599	0.942
	60	29.730	2.442	0.942
	80	8.120	1.919	0.966
wool-g-t	20	34.63	2.211	0.922
	40	36.98	2.162	0.939
	60	72.88	2.768	0.877
	80	65.14	2.374	0.907
NW	20	15.65	1.472	0.985
	40	18.35	1.543	0.979
	60	14.92	1.467	0.987
	80	22.60	1.644	0.975

3.4.3. Jossens model

The third isotherm equation used in this study is the Jossens isotherm which considered as a combination of Langmuir and Freundlich models. It approaches the Freundlich model at high concentration and is in accord with the low concentration limit of the Langmuir equation (Kumar et al., 2010). The Jossens equation is given as follows:

$$Y_e = \frac{i.C_e}{1 + j.(C_e)^m} \quad (9)$$

Where i ($L.g^{-1}$), j ($L.mg^{-1}$) and m are the jossens constants that may be obtained from the adsorption data via an iterative procedure using a computer program. Table 4 displayed the results of the calculated isotherm constants at different temperatures.

On the basis of the correlation coefficients (R^2), the Jossens model showed the highest R^2 values ($0.995 < R^2 < 0.999$) over the whole temperature range studied. This implied that the adsorption of AY 17 onto NW, wool-g-t and [metal/ wool-g-t] supports could be better described by the Jossens model than by the other isotherms.

Table 4 also revealed that values of j are very near to zero, suggesting that the extent of adsorbed dye depends only on the concentration of dye introduced in bath. In this case the adsorption is named linear (El Ghali et al., 2010).

Table 4: Jossens Constants for Adsorption of AY 17 onto NW, wool-g-t and [metal/wool-g-t] adsorbents

Adsorbent	T (°C)	i	j	m	R ²
Cu(II)/wool-g-t	20	7.710	0.00027	1.178	0.995
	40	5.013	0.00022	1.529	0.998
	60	4.249	0.00006	1.716	0.999
	80	3.539	0.00006	1.686	0.999
Fe(III)/wool-g-t	20	4.363	0.00014	1.540	0.997
	40	3.824	0.00015	1.538	0.999
	60	3.141	0.00018	1.510	0.999
	80	2.428	0.00031	1.416	0.999
Co(II)/ wool-g-t	20	4.236	0.00054	1.325	0.998
	40	2.763	0.00061	1.315	0.999
	60	2.011	0.00022	1.419	0.999
	80	0.716	0.00001	1.717	0.999
wool-g-t	20	3.122	0.00003	1.795	0.997
	40	3.795	0.00008	1.661	0.999
	60	5.292	0.00015	1.618	0.998
	80	6.270	0.00008	1.744	0.998
NW	20	4.033	0.00002	1.809	0.999
	40	4.078	0.00001	1.925	0.999
	60	3.834	0.00003	1.785	0.999
	80	4.445	0.00006	1.692	0.999

4. CONCLUSION

A novel metal ion-imprinted chemically modified wool chelating fibers (wool-g-t) were prepared in this work. The synthesized support was then saturated with Cu(II), Co(II) and Fe(III) ions. Further, the resulting materials were characterized using FTIR analysis. Afterwards, the [metal/ wool-g-t] complexes as well as the unmodified and the modified fibers were used for the removal of AY 17 from aqueous solutions. It was found that the binding of modified wool fibers with the different metal ions has increased the amount of the selected dye uptake. The equilibrium data have been analyzed using Langmuir, Freundlich and Jossens isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been evaluated and the equilibrium data were well described by the Jossens model. The analysis of the thermodynamic parameters revealed that these later were depended on the type of adsorbent utilized.

REFERENCES

- Akhtar, M., Hasany, S. M., Bhangar, M.I., Iqbal, S. (2007).** Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions. *Chemosphere*, Vol. 66, 1829-1838.
- Anirudhan, T.S., Rejeena, S.R. (2013).** Poly(methacrylic acid-co-vinyl sulfonic acid)-grafted-magnetite/nanocellulose superabsorbent composite for the selective recovery and separation of immunoglobulin from aqueous solutions. *Separation and Purification Technology*, Vol. 119, 82-93.

- Ardejani, F. D., Badii, Kh., Limaee, N. Y., Shafaei, S.Z., Mirhabibi, A.R. (2008).** Adsorption of Direct Red 80 dye from aqueous solution onto almond shells: Effect of pH, initial concentration and shell type. *Journal of Hazardous Materials*, Vol. 151, 730-737.
- Areco, M. M., Afonso, M. S. (2010).** Copper, zinc, cadmium and lead biosorption by *Gymnogongrus torulosus*. Thermodynamics and kinetics studies. *Colloids and Surfaces A*, Vol. 81, 620-628.
- Barros, S. T. D., Santos, O. A.A. (2010).** Biosorption of reactive blue 5G dye onto drying orange bagasse in batch system: Kinetic and equilibrium modeling. *Chemical Engineering Journal*, Vol. 163 (1-2) 68-77.
- Chakraborty, S., Chowdhury, S., Saha, P.D. (2011).** Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk. *Carbohydrate Polymers*, Vol. 86, 1533-1541.
- Chen, S., Yue, Q., Gao, B., Xu, X. (2010).** Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue. *Journal of Colloid and Interface Science*, Vol. 349, 256-264.
- Chowdhury, S., Mishra, R., Saha, P., Kushwaha, P. (2011).** Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. *Desalination*, Vol. 265, 159-168.
- Crini G., Badot P.M. (2008).** Application of chitosan, a natural aminopolysaccharide for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. *Progress in Polymer Science*, Vol. 33, 399-447.
- Derrouiche, I., Moussa, A., Ben Marzoug, I., Sakli, F., Roudesli, S. (2015).** The effect of deposit zeolites zsm-5 onto date palm fibers on curing cationic dyes decolorization. *The International Journal of Applied Research on Textile*, Vol. 3, N°1, 69-78.
- El Ghali, A., Baouab, M. H. V, Roudesli, M. S. (2010).** Stipa Tenacissima L Cationized Fibers as Adsorbent of Anionic Dyes. *Journal of Applied Polymer Science*, Vol. 116, 3148-3161.
- El Ghali, A., Baouab, M. H. V, Roudesli, M. S. (2011).** Preparation, characterization and application of a [copper (II)/ethylenediamine–cotton] complex for the removal of AB25 from aqueous solution in a laboratory scale column. *Chemical Engineering Journal*, Vol. 174, 18-26.
- El Qada, E. N., Allen, S. J., & Walker, G. M. (2008).** Adsorption of basic dyes from aqueous solution onto activated carbons. *Chemical Engineering Journal*, Vol. 135, N°3, 174-184.
- Feng, N., Guo, X., Liangn, S. (2009).** Adsorption study of copper (II) by chemically modified orange peel. *Journal of Hazardous Materials*, Vol. 164, 1286-1292.
- Fiorentin, L., Trigueros, D. D. E.G., Módenes, A. N., Espinoza-Quiñones, F. R., Pereira, N. C., Freddi, G., Arai, T., Colonna, G.M., Boschi, A., Tsukada, M. (2001).** Binding of metal cations to chemically modified wool and antimicrobial properties of the wool–metal complexes. *Journal of Applied Polymer Science*, Vol. 82, 3513-3519.
- Ghaedi, M., Sadeghian, B., Pebdani, A. A., Sahraei, R., Daneshfar, A., & Duran, C. (2012).** Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon. *Chemical Engineering Journal*, Vol. 187, N°1, 133-141.
- Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y., & Zou, L. (2008).** Use of rice husk for adsorption of congo red from aqueous solution in column made. *Bioresource Technology*, Vol.99, 2938-2946.
- Jiugang, Y., Qiang, W., Ping, W., Li, C., Xuerong, F. (2012).** Promotional effect of 1-butyl-3-methylimidazolium chloride ionic liquid on the enzymatic finishing of wool. *Engineering in Life Sciences*, Vol. 12, N°2, 209-2015.
- Kul A. R., Koyuncu H. (2010).** Adsorption of Pb(II) ions from aqueous solution by native and activated bentonite: Kinetic, equilibrium and thermodynamic study. *Journal of Hazardous Materials*, Vol. 179, 332-339.

- Kumar, P. S., Ramalingam, S., Senthamarai, C., Niranjanaa, M., Vijayalakshmi, P., Şener, S. (2008).** Use of solid wastes of the soda ash plant as an adsorbent for the removal of anionic dyes: Equilibrium and kinetic studies. *Chemical Engineering Journal*, Vol. 138, 207-214.
- Li, Q., Yue, Q. Y., Su, Y., Gao, B. Y., Sun, H. J. (2010).** Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite. *Chemical Engineering Journal*, Vol. 158, 489-497.
- Liu, S., Sun, H., Liu, S., & Wang, S. (2013).** Graphene facilitated visible light photodegradation of methylene blue over titanium dioxide photocatalysts. *Chemical Engineering Journal*, Vol. 214, N°1, 298-303.
- Mayur, B. K., Tatoba, R. W. Swapnil, M. P., Byong-Hun, J., & Sanjay, P. G. (2017).** Monitoring the gradual biodegradation of dyes in a simulated textile effluent and development of a novel triple layered fixed bed reactor using a bacterium-yeast consortium. *Chemical Engineering Journal*, Vol. 307, N°1, 1026-1036.
- Monier M., Nawar N., Abdel-Latif D.A. (2010).** Preparation and characterization of chelating fibers based on natural wool for removal of Hg(II), Cu(II) and Co(II) metal ions from aqueous solutions. *Journal of Hazardous Materials*, Vol. 184, 118-125.
- Ofomaja A.E., Ho Y.S. (2007).** Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent. *Journal of Dyes and Pigments*, Vol. 74, 60-66.
- Sivanesan, S. (2010).** Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*, Vol. 261, 52-60.
- Susmita, S. G., Bhattacharyya, K. (2008).** Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. *Journal of Environmental Management*, Vol. 87, 46-58.
- Taddei, P., Monti, P., Freddi, G., Arai, T. (2003).** M. Tsukada, Binding of Co(II) and Cu(II) cations to chemically modified wool fibres: an IR investigation. *Journal of Molecular Structure*, Vol. 650, 105-113.
- Wan, A., Yu, W. (2011).** Effect of wool fiber modified by ecologically acceptable ozone-assisted treatment on the pilling of knit fabrics. *Textile Research Journal*, Vol. 82, N°1, 27-36.
- Wang, S., Li, H. (2005).** Dye adsorption on unburned carbon: Kinetics and equilibrium. *Journal of Hazardous Materials B*, Vol. 126, 71-77.
- Yao, T., Guo, S., Zeng, C., Wang, C., & Zhang, L. (2015).** Investigation on efficient adsorption of cationic dyes on porous magnetic polyacrylamide microspheres. *Journal of Hazardous Materials*, Vol. 292, 90-97.
- Yeap, K. L., Teng, T. T., & Poh, B. T. (2014),** Norhashimah Morad, Khai Ern Lee, Preparation and characterization of coagulation/flocculation behavior of a novel inorganic-organic hybrid polymer for reactive and disperse dyes removal. *Chemical Engineering Journal*, Vol. 243, N°1, 305-314.
- Yuan, J., Wang, Q., Fan, X. Wang, P. (2010).** Enhancing dye adsorption of wool fibers with 1-butyl-3-methylimidazolium chloride ionic liquid processing. *Textile Research Journal*, Vol. 80, N°18, 1898-1904.
- Zheljazkov, V.D., Stratton, G.W., Pincock, J., Butler, S., Jeliaskova, E.A., Nedkov, N.K., Gerard, P.D. (2009).** Wool-waste as organic nutrient source for container-grown plants. *Waste Management*, Vol. 29, 2160-2164.