Human hair as a biosorbent to uptake some dyestuffs from aqueous solutions

M.A. Hashem, R.M. Abdelmonem and T.E. Farrag
Chemical Eng. Dept., Faculty of Eng., El-Minia University, El-Minia, Egypt

Human hair waste has been investigated as an adsorbent for the removal of Basic Blue 69 and Acid Blue 25 dyestuffs from aqueous solutions. Batch experiments were carried out to determine the effects of contact time on this adsorption process where, it was found that the uptake of dyes was virtually complete after 100 minutes. The maximum adsorption capacity (q_{max}) of BB 69 and AB 25 onto untreated human hair was 16.9 mg/g and 5.4 mg/g respectively. Equilibrium isotherms have been determined for both dyes where, L-shaped adsorption isotherms were obtained. The experimental results have been fitted with the Langmuir, Freundlich and Redlich-Peterson models. It is clear from the results that the Freundlich model fits the experimental data significantly better than the Langmuir and Redlich-Peterson models.

الهدف من هذا البحث هو دراسة إمكانية استخدام مخلفات شعر الانسان (بدون معالجة) كمادة مازة للأصباغ من المحاليل المائية. وقد استخدم فى الدراسة نوعين من الصبغات وهما صبغة قاعدية زرقاء وصبغة حامضية زرقاء. وفى بداية الدراسة تم تحديد الوقت اللازم لعملية الاتزان ووجد انه ١٠٠ دقيقة.وبعد ذلك تم دراسة التوازنات ثابتة درجة الحرارة ومنها أمكن الحصول على السعة القصوى للمادة المازة وكانت كالتالى: بالنسبة للصبغة القاعدية الزرقاء (mg/g 16.9) أما بالنسبة للصبغة الحامضية الزرقاء فكانت (mg/g 5.4). وقد تم اختبار النتائج المعملية مع النماذج الرياضية المعروفة فى مجال الاتزان ووجد انها تتطابق مع بعض هذه النماذج ولكنها تتطابق بشكل جيد مع نموذج فرندلك. وقد خلصت الدراسة المعملية الى انه يمكن استخدام مخلف شعر الانسان كمادة مازة (رخيصة جدا) لازالة بعض الاصباغ من المحاليل المائية ، ولكن الدراسة توصى بمزيد من البحث بأن تجرى معالجة بأى وسيلة من وسائل التنشيط المعروفة لتنشيط الشعر لزيادة السعة القصوى للمادة المازة

Keywords: Human hair, Dyestuff, Adsorption isotherms

1. Introduction

Water is a basic need of life and is used in many ways to cater the needs of daily life, so the control of water pollution is one of today's major of scientific activity. In recent years drinking water has become a major issue for public and political debate. One area that has received close attention is that of dyestuffs.

The untreated textile processing effluents are very toxic, since they contain a large number of metal complex dyes (e.g. Cr or Co complexes) [1]. The high concentration of such dyes causes many waterborne diseases and increases the Biological Oxygen Demand (BOD) of the receiving waters. Because of their complex structure and large molecular size, most dyestuffs are considered as difficult for removal by conventional, biological and physical treatment methods [2].

The adsorption technique has been found to be a useful means for controlling the extent of water pollution due to dyes and metallic species [3]. The major advantages of an adsorption system for water pollution control are less investment in terms of both initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared with conventional biological treatment processes.

Most work on adsorption to date has been undertaken using activated carbon, which has found wide application in wastewater treatment operations. Other materials studied for adsorbing dyestuffs are activated silica, activated alumina [4], peat [5], wood [6], chitin [7], bagasse pith [8] and maize cob [9]. To date, no other adsorbent has proved as versatile as activated carbon. It has been reported that it is capable of removing specific contaminants and is, therefore, likely to make significant contributions to water purification in the future.

Biosorbents have caught the attention of many researchers for the removal of heavy

metals as environmental contaminants from aqueous solutions, with an abundant literatures existing with respect to such processes. For example, spent animal boned have been used for the removal of copper and zinc [10], lignite for the removal of mercury, cadmium and lead [11], immobilized fungal biomass for the removal of different metal ions [12], and peanut hulls for the removal of the cadmium [13]. Human hair has also been used as a biosorbent for the removal of different metal ions [14]. The uptake of metal ions by thesae materials was attributed to their constituents which contain such functional groups as carboxy, hydroxyl, phosphate and amine that act as binders for these ions. In contrast, literature on the use of biosorbents for the removal of dyestuffs is very limited and there is no one in the use of human hair.

Human hair is made of a fibrous proteinaceous material known as keratin that has a complicated structure and contains a large surface area. As mentioned earlier, with and without chemical treatment, human hair has been showed to be a good biosorbent for metal ions [14]. The use of such human hair waste as an adsorbent would help to reduce the cost of wastewater treatment and would make a contribution in cleaning the environment.

In the present work, the ability of human hair not subject to chemical treatment as an biosorbent for dyestuffs has been examined. Human hair was chosen because it is abundant human waste of no commercial use. The work is directed primarily towards studying the adsorption isotherms. The isotherm data have been analysed using three models, viz. the Langmuir, Freundlich and Redlich-Peterson. A comparison of the experimental data with theoretical isotherms have been studied in order to develop a model which both accurately represents the experimental adsorption results and could be used for design purposes.

2. Materials and methods

The adsorbent used in this investigation is human hair waste not subject to chemical treatment. Human hair waste collected from various local barber shops, were mixed together, washed, clean of the adhering dirt with a detergent, rinsed several times with distilled water and finally dried in an air oven at 100 °C before being used in the adsorption experiments.

The adsorbates (dyestuffs) and their structures used in the experiments are listed blow. The dyestuffs are used as the commercial salts and were supplied by Bayer.

2.1. Basic blue 69, BB69 (astrazone blue FRR as supplied)

No structure is available for this dye. It belongs to the methane class of which chromophore is a conjugate chain atoms terminated by an ammonium group, and in addition a nitrogen, sulpher or oxygen atom, or an equivalent unsaturated group. A general structure of methane group is
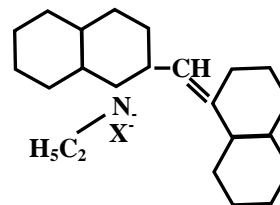
2.2. Acid blue 25, ab25 (telon blue anl as supplied)
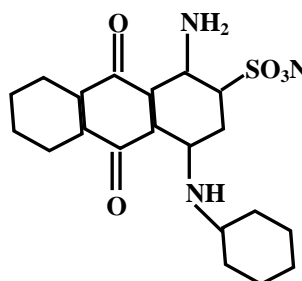
The dye was makeup in stock solution of concentration 1000 mg/dm³ and was subsequently diluted to require concentration using distilled water. The concentrations of the dye staffs in aqueous solution were determined using a spectrophotometer (Spectro-Plus MK1A). All measurements were made at the wave length corresponding to maximum absorbance, λ_{max}, which was 585 nm for BB 69 and 600 nm for AB 25. In accordance with the Lambert-Bear law the absorbance was found to vary linearly with

concentration and a dilution of concentrated samples were undertaken when the absorbance exceed 0.6 to give accurate results.

Adsorption isotherms were determined using the bottle- point method. The adsorption capacity of the human hair for dyes was determined by shaking a constant mass (0.5 g) of human hair with a fixed volume of 0.05 dm^3 of dye solution, in a range of concentrations. All experiments were carried out at 25±1 °C to eliminate any temperature effects using temperature controlled water bath.

3. Results and discussion

3.1. Effect of contact time and concentration

Preliminary tests were undertaken to assess the contact time necessary for each system to come to equilibrium, and for experimental purposes, each system was given a contact time in excess of this period. So such information may be used to predict experimental conditions required to perform adsorption isotherms.

A series of contact experiments was undertaken at varying initial dye concentrations of 400 and 600 mg.dm^{-3} for BB 69 and 200 and 400 mg.dm^{-3} for AB 25. figs. 1 and 3 show that a rapid increase of dye adsorption occurred in all cases at low solid-phase concentrations (early stages of contact time) which may be attributed to surface mass transfer [16]. Figs. 1 and 3 also show that the amount of dye adsorbed from aqueous solutions increased with time, where equilibrium being achieved within 100 min. at 25±1 °C. The plots of adsorption versus time for both dyes depicted in both figures are smooth and continuous, indicating mono layer coverage of dye on the surface of the adsorbent. However, the percentage of the dye adsorbed by the adsorbent decreased with increasing dye concentration. The average removal of saturation was found to be 39.5% and 29.2% for 400 and 600 mg dm^{-3} initial concentrations of BB 69 respectively as shown in fig. 2, compared to 19% and 12.2% for 200 and 400 mg dm^{-3} initial concentrations of AB 25 respectively as shown in fig. 4.
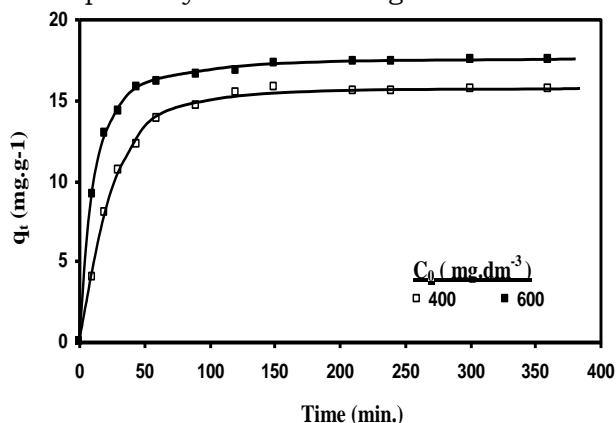
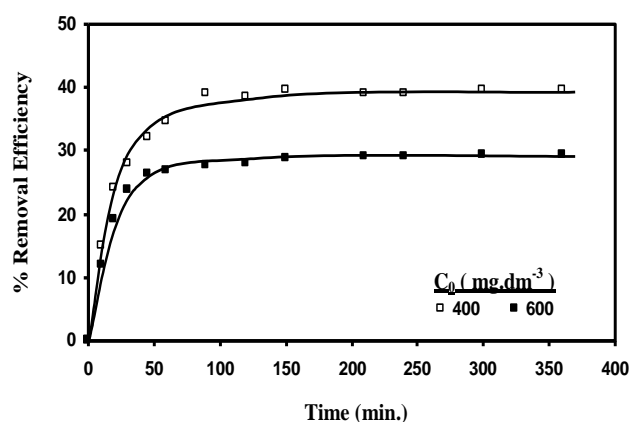Fig.1. Equilibrium time for the adsorption of BB69 onto natural human hair.

Fig. 2. Effect of initial concentration on the removal of BB69 by adsorption onto natural human hair.
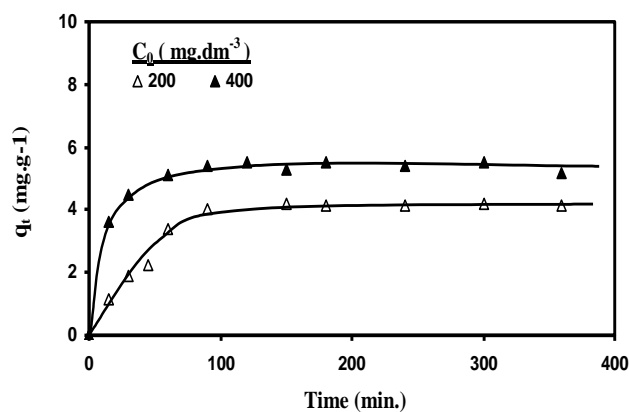

Fig. 3. Equilibrium time for the adsorption of AB25 onto natural human hair.
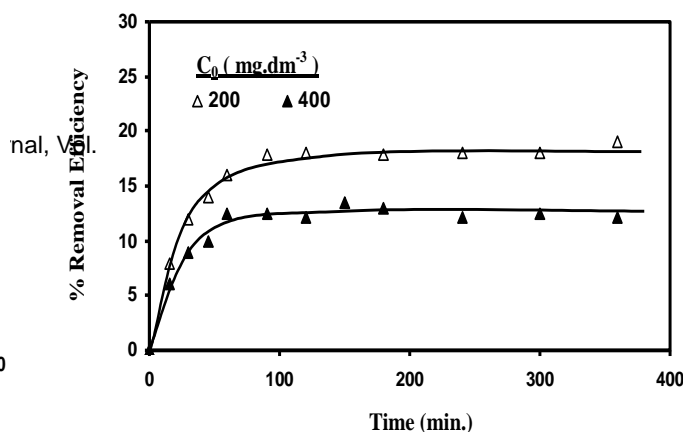
Fig. 4. Effect of initial concentration on the removal of AB25 by adsorption onto natural human hair.

3.2. Equilibrium isotherm

The purpose of studying adsorption isotherms is, firstly, to measure the adsorption capacity of each system and secondly, to ascertain the liquid-solid equilibrium distribution of the solute concerned. The distribution of dyestuff between the adsorbent and the liquid phase, when the system is in a state of equilibrium, is important to establish the capacity of the adsorbent for dye. Preliminary experiments showed that such equilibrium was established within 100 minutes. However, all equilibrium experiments were allowed to run for 150 minutes.

Fig. 5 depicts the adsorption isotherms for the two dyestuffs. According to the classification of Giles et al., [16-17], the adsorption isotherms obtained may be classified as L-type. In this case, adsorption is very efficient at low concentration, but it becomes increasingly difficult, as the concentration increases, for a solute molecule to find a vacant adsorption site.

Analysis of such isotherm data is important in order to develop a model which both accurately represents the experimental adsorption results and could be used for design purposes. Several isotherm models are available for this analysis. In this study three of these have been selected to simulate the experimental data, namely the Langmuir, Freundlich and Redlich-Peterson isotherms.
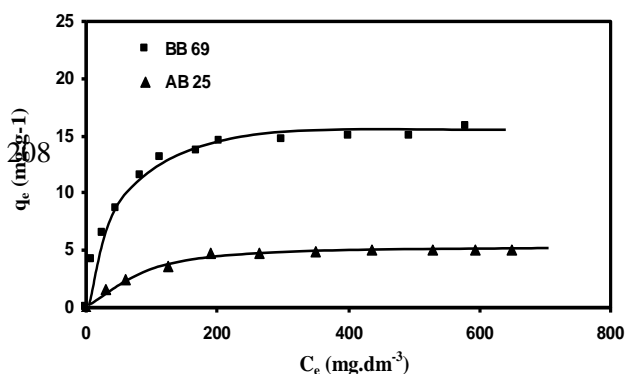
Fig. 5. Adsorption isotherms for BB 69 and AB 25 onto natural human hair.
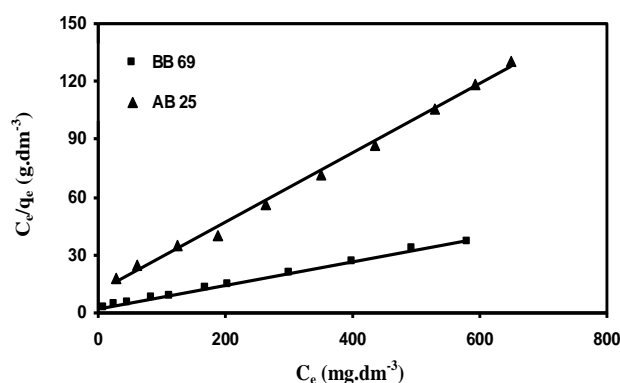

Fig. 6. Langmuir plot for the adsorption of BB 69 and AB 25 onto natural human hair.

The first isotherm tested was that of the Langmuir which may be represented by the equation:

$$q_e = (K_L.C_e)/(1 + a_L.C_e). \qquad (1)$$

This may be converted into a linear form convenient for plotting and determining the constants, K_L and a_L:

$$C_e/q_e = (1/K_L) + (a_L/K_L)\,C_e. \qquad (2)$$

The plots of C_e/q_e against C_e for both dyes are shown in fig. 6 and are fit to be linear over a certain concentration range. Linear plots of C_e/q_e against C_e suggest the applicability of the Langmuir isotherm for the present system, and demonstrate monolayer coverage of the adsorbate at the outer surface of the adsorbent [3].

Table 1
Estimated parameters of the Langmuir model.

Dye	K_L (dm³/g)	a_L (dm³/mg)	$q_{max.}$ (mg/g)	$\overline{R}$ (-)	Correlation Coefficient
BB69	0.389	0.023	16.9	0.72	0.94
AB25	0.097	0.018	5.4	0.91	0.93

Values of K_L and a_L have been calculated using the least-squares method and are tabulated in table 1. The values of constant K_L/a_L are important since they represent the maximum or monolayer adsorption capacity (q_{max}) of the natural human hair waste for a particular dyestuff.

The influence of the isotherm shape on whether adsorption is favorable or unfavorable has been considered. For a Langmuir-type adsorption process the isotherm shape can be classified by the dimensionless equilibrium parameter, $\overline{R}$, given in eq. (3):

$$\overline{R} = 1/(1 + a_L . C_0). \tag{3}$$

The equilibrium parameter indicates the shape of the isotherm as follows:

Values of $\overline{R}$	Types of isotherms
$\overline{R} > 1$	Unfavourable
$\overline{R} = 1$	Linear
$0 < \overline{R} < 1$	Favourable
$\overline{R} = 0$	Irreversible

Values of $\overline{R}$ for BB 69-hair and AB 25-hair systems have been calculated and are tabulated in table 1. The values of $\overline{R}$ are depicted in fig. 7, which is a plot of the dimensionless solid-phase concentration, Q_e, against the dimensionless liquid-phase concentration, X_e for each system. The general relationship for the equilibrium parameter ($\overline{R}$) for any isotherm is:

$$\overline{R} = X_e (1 - Q_e) / Q_e (1 - X_e), \tag{4}$$

where,

$$X_e = C_e/C_{ref} \text{ , and } Q_e = q_e/q_{ref}$$

For a single solute adsorption system, C_{ref}, is usually the highest liquid-phase concentration encountered and q_{ref} is the equilibrium solid-phase concentration co-existing with C_{ref}. Substituting eq. (4) into eq. (3) and simplifying, eq. 3 becomes:

$$\overline{R} = 1 / (1 + a_L . C_{ref}). \tag{5}$$

Since C_{ref} is the highest liquid-phase concentration encountered (i.e. $C_{ref} = C_0$), it follows that eqs. (3) and (5) are identical. The degree of "favorability" is generally related to the reversibility of the system. Indeed, the degree of reversibility of the dye-hair systems are, $0 < \overline{R} < 1$, which represents the reversible isotherm case in the favorable range.

The experimental equilibrium data for the adsorption of BB 69 and AB 25 onto natural human hair have also been analyzed using the Freundlich isotherm as given by eq. (6).

$$q_e = K_F . C_e^{1/n} . \tag{6}$$

The equation may be linearized via a logarithmic plot which enables the exponent, n, and the constant, K_F, to be determined from eq. 7.
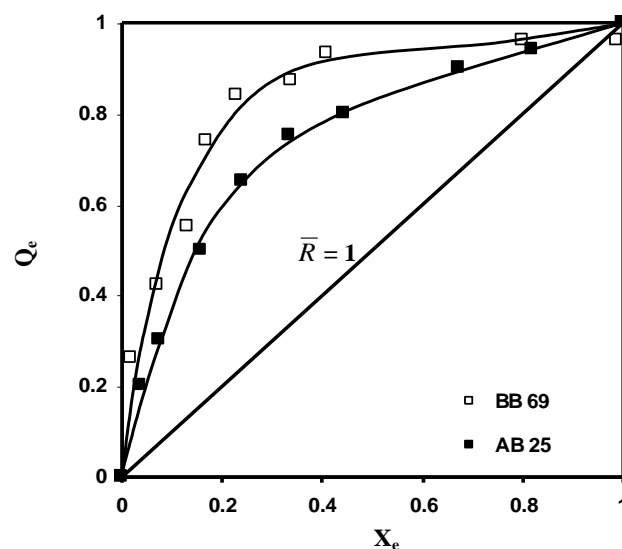

Fig. 7. Equilibrium parameter plot for the adsorption of BB 69 and AB 25 onto natural human hair.

$$\log q_e = \log K_F + (1/n) \log C_e . \quad (7)$$

Inspection of the results derived from the Freundlich analysis and depicted by eq. (7) shows that a plot of log q_e versus log C_e exhibits some curvature. Indeed, the results can be better represented by more than one straight line [18]. A general equation for the entire concentration range may be expressed as:

$$q_e = K_{F,i} . C_e^{1/n_i} . \quad (8)$$

Fig. 8 shows the Freundlich isotherms for both dyes on the basis of eq. 8. The Freundlich parameters, K_F and n have been calculated using the least-squares method applied to the straight lines shown in fig. 8 and are listed in table 2 together with the appropriate concentration ranges and the correlation coefficients obtained.

Two important conclusions can be derived from the data presented in table 2 that the Freundlich model successfully describes the adsorption isotherm of the BB 69 and AB 25 over a wide concentration range and suggests that the adsorption sites were not saturated at any of the concentration considered in this study. The magnitude of exponent, **n**, gives an indication of the favorability and capacity of the adsorbent-adsorbate system. Values of **n** > 1, represent favorable adsorption according to Treybal [19]. In this work the values of **n** are greater than one (**n** > 1) for both sections of plot which indicates that the dyes show favorable adsorption by natural human hair.

Another isotherm which incorporates intermediate terms between the Langmuir and Freundlich equations describes the isotherm better than the classical isotherm models because of its mathematical flexibility. The Redlich-Peterson isotherm has been used in this work and is represented by the eq. (9):

$$q_e = (K_{RP} . C_e) / (1 + a_{RP} . C_e^{\beta}) . \quad (9)$$

For β=1, eq. (9) converts to the Langmuir isotherm; and for $1 < (a_{RP} . C_e^{\beta})$ it is identical with the Freundlich isotherm. The linear form is shown in eq. (10) from which the constants,

K_{RP}, a_{RP} and β, which characterize the isotherm, can be determined:

$$\log \{(K_{RP} . C_e / q_e)\text{-}1\} = \log a_{RP} + \beta \log C_e . \quad (10)$$

The plot of log $\{[K_{RP} . C_e / q_e] - 1\}$ against log C_e is shown in fig. 9 and is seen to fit linear over a certain concentration range. The Redlich-Peterson parameters have been calculated using an iterative computer program for data fitting and minimizing the correlation coefficient, and are tabulated in table 3.

3.3. Comparison of theoretical isotherms with experimental results

Using the appropriate constants of the Langmuir, Freundlich and Redlich-Peterson models, the theoretical isotherm curves were predicted using known values of C_e. Figs. 10 and 11 show a comparison of the experimental points with the Langmuir, Freundlich and Redlich-Peterson models, in order to establish which model yields the "best fit". Both dyes showed little significant difference between the three isotherm models. This means that each equation was able to adequately predict the equilibrium behavior, but the Freundlich models gave good agreement with the experimental data for the two dyestuffs.
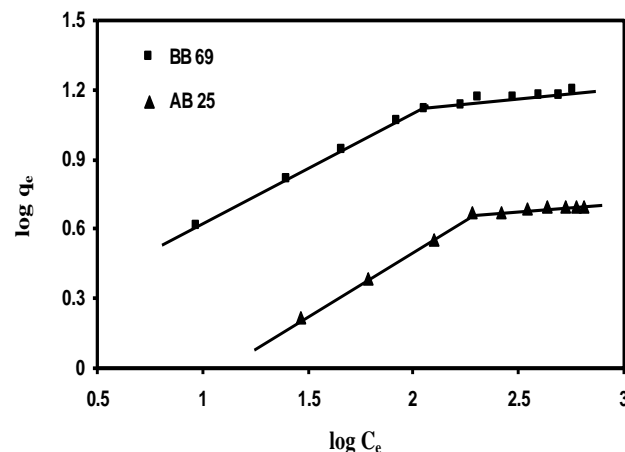

Fig. 8. Freundlich plot for the adsorption of BB 69 and AB 25 onto natural human hair.

Table 2
Estimated parameters of the Freundlich model.

Dye	First section of plot				Second section of plot			
	K_F (dm³/g)	n (-)	C.R. (mg/dm³)	Corr. coeff.	K_F (dm³/g)	n (-)	C.R. (mg/dm³)	Corr. coeff.
BB 69	1.44	2.14	9.4-113.3	0.99	8.58	10.69	113.3-580	0.95
AB 25	0.25	1.79	29.3-189.3	0.98	3.32	15.46	189.3-650	0.94

C.R. Concentration Range.

Table 3
Estimated parameters of the Redlich-Peterson model.

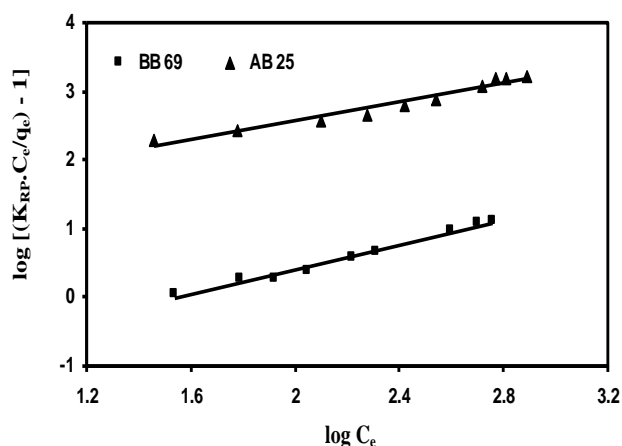| Dye	K_{RP} (dm³/g)	a_{RP} (dm³/g)$^{1/\beta}$	β (-)	Correlation Coefficient
BB 69	0.390	3.557	0.92	0.98
AB 25	0.097	0.031	0.90	0.97

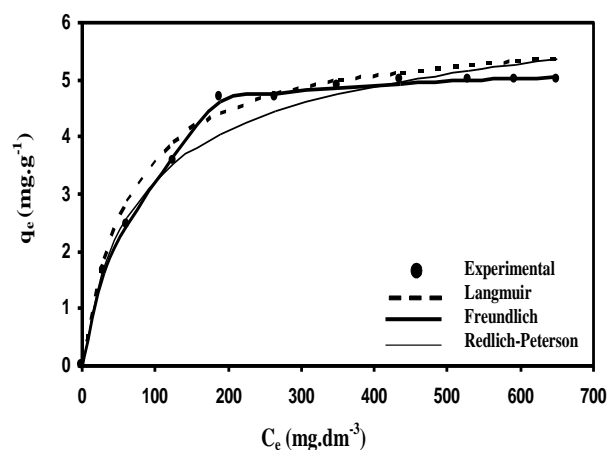Fig. 9. Redlich-Peterson plot for the adsorption of BB 69 and AB 25 onto natural human hair.

Fig. 11. Comparison of theoretical isotherm plots with experimental data for the adsorption of AB 25 onto natural human hair.
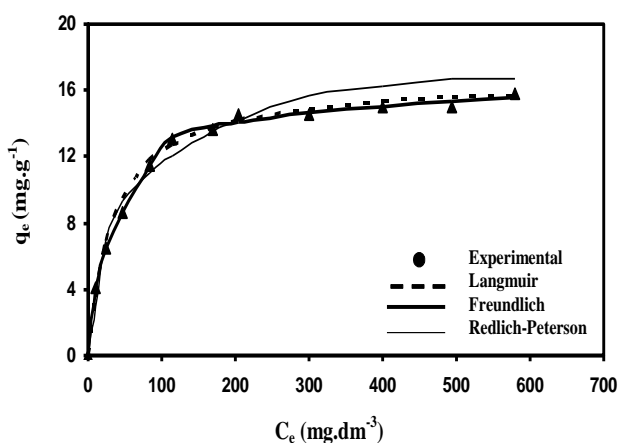

Fig. 10. Comparison of theoretical isotherm plots with experimental data for the adsorption of BB 69 onto natural human hair.

4. Conclusions and recommendations

The utilization of human hair waste for the removal of basic dye (Basic Blue 69) and acidic dye (Acid Blue 25) from aqueous solutions was investigated experimentally. Although the samples were left to equilibrate for 400 min., the rate of dyes uptake was almost complete after 100 min. The experimental results obtained indicate that the natural human hair has an ability to adsorb considerable quantities of basic dye, namely 16.9 mg/g for Basic Blue 69. Lower capacity was obtained with the acid dye, namely 5.4 mg/g for Acid Blue 25. Difference in adsorption abilities of dyestuffs under study may be due to the relation between their

functional chemical constitution and that of the proteinacous adsorbent used.

Equilibrium isotherms have been determined for both dyestuffs and the data obtained correlated using equations based on the Langmuir, Freundlich and Redlich-Peterson models. Equilibrium parameter ($\overline{R}$) was used to assess the nature of the equilibrium for dyestuffs and the results indicated that the two dyestuffs exhibit "favorable" adsorption onto natural human hair. Theoretical isotherms were compared with experimental data and the general results of this study reveal that the Freundlich isotherm better fitted the experimental adsorption data since the correlation coefficients obtained from its plots were higher overall than those obtained from the other models. The present study confirms the capability of human hair for the removal of organic pollutants such as some members of dyestuffs from aqueous solutions and opens the door for further research designed to increase this capability by chemical treatment for human hair (activation process).

Nomenclature:

a_L is the parameter of Langmuir isotherm (dm^3/mg)

a_{RP} is the parameter of Redlich-Peterson isotherm [$(dm^3/mg)^{1-\beta}$]

C_0 is the initial liquid-phase concentration (mg/dm^3)

C_e is the equilibrium liquid-phase concentration (mg/dm^3)

C_{ref} is the reference liquid-phase concentration (mg/dm^3)

K_F is the parameter of Freundlich isotherm (dm^3/g)

K_L is the parameter of Langmuir isotherm (dm^3/g)

K_{RP} is the parameter of Redlich-Peterson isotherm (dm^3/g)

n is the Freundlich exponent (dimensionless)

Q_e is the dimensionless solid-phase concentration at equilibrium

q_e is the equilibrium solid-phase concentration (mg/g)

q_{ref} is the reference solid-phase concentration at onset of monolayer coverage (mg/g)

$\overline{R}$ is the dimensionless equilibrium parameter, defined by eq. (5)

X_e is the dimensionless liquid-phase concentration at equilibrium

Greek symbols

β is the Redlich-Peterson exponent (dimensionless)

λ_{max} is the wavelength of light at which absorption is a maximum (nm)

References

[1]   M. Ajmal, and A.U. Khan, Environ. Pollut. Ser., p. 131, A37 (1985).

[2]   V.J.P. Poots, G. McKay, and J.J. Healy, J. Water Pollut. Control Fed., p. 926, 5 (1978).

[3]   K.K. Panday, G. Prasad, and V.N. Singh, Water, Air, Soil Pollut., p. 287, 27 (1986).

[4]   F. Alexander, V.J.P. Poots, and G. McKay, End. Eng. Chem. Fundam., p. 406, 17 (1978).

[5]   G. McKay, S.J. Allen, I.F. McConvey, and M.S. Otterburn, J. Colloid Interface Sci., p. 323, 80 (1981).

[6]   M.S. El-Gundi, M.Sc. Thesis, Minia University, (1983).

[7]   G. McKay, S.J. Allen, and J.R. Gardner, J. Appl. Polym. Sci. Vol. 27, p. 3043, (1982).

[8]   M.S. El-Gundi, Ph. D. Thesis, The Queen's University of Belfast (1987).

[9]   M.S. El-Gundi, Adsorption Sci and Technology, Vol. 3, p. 114 (1990).

[10] S. Al-Asheh, F. Banat, and F. Mohi, Chemosphere, Vol. 39, p. 2097 (1994).

[11] A. Christian, et al., Chem. Eng. Technol, Vol. 22, p. 45 (1999).

[12] A. Coppor, and T. Virarghavn, Water Res., Vol. 32, p. 1968 (1998).

[13] K. Periasamy, and C. Namasivayan, Ind. Eng. Chem. Res., Vol. 32, p. 317 (1994).

[14] T.C. Tan, C. K. Chia and C.K. Teo, Water Res., Vol. 19, p. 157 (1985).

[15] G. McKay and A.G. Sweeney, Water Air Soil Pollut, Vol. 3, p. 14 (1980).

[16] C.H. Giles, D. Smith and A. Huitson, J. Colloid Interface Sci., Vol. 47, p. 755, (1974a).

[17] C.H. Giles, A.P. D'Silva and A. Huitson, J. Colloid Interface Sci., Vol. 47, p. 766, (1974b).

[18] W. Fritz, W. Merk, and E.U. Schlunder, Chem. Eng. Sci., Vol. 36, p. 731 (1981).

[19] R.E. Treybal, Mass Transfer Operation. McGraw-Hill, Singapore, 3th ed., p. 182. (1985).