Removal of Eosin Y, an Anionic Dye, from Aqueous Solutions Using Conducting Electroactive Polymers

Reza Ansari* and Zahra Mosayebzadeh

Chemistry Department, Faculty of Science, University of Guilan,
P.O. Box: 41335-1914, Rasht, Iran

A B S T R A C T

Polypyrrole (PPy) and polyaniline (PAni) conducting polymers were synthesized chemically on the surface of wood sawdust (SD) to remove Eosin Y (EY), an anionic dye, from aqueous solution. The important parameters such as pH, initial concentration, sorbent dosage and contact time on uptake of EY solution were also investigated. The experiments were carried out using both batch and column systems at room temperature. It was found that both polymers can be used to remove anionic dyes such as EY from aqueous solutions very efficiently. The sorption process of EY dye using both polypyrrole and polyaniline coated onto sawdust (respectively termed as PPy/SD and PAni/SD) was less dependent on the pH of the solutions at least at pH values from 2-10. Considerable decrease in sorption performance occurred only at high pH values (pH $\geq$ 12). According to our "breakthrough analysis", it was found that PAni/SD adsorbent is more efficient for EY removal in flow or column system. Adsorption of EY on the PPy/SD and PAni/SD under different conditions was examined by pseudo-first-order and pseudo-second-order models, and their respective rate constants of first-order adsorption (k_1) and second-order adsorption (k_2) were estimated. The experimental data fitted very well into pseudo-second-order kinetic model. The experimental data were also analyzed by the Langmuir and Freundlich models of adsorption. Based on the correlation coefficient values obtained (R^2), it was found that equilibrium data fitted well with both models. In order to find out the possibility of desorption for frequent use, the chemical regeneration of the employed adsorbents was also investigated. It was found that more than 96% of the EY dye can be recovered from PPy/SD column using a dilute NaOH solution (0.05 M).
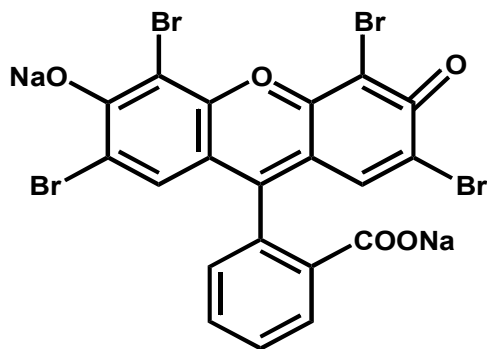
(∗) To whom correspondence to be addressed.
E-mail: ransari@guilan.ac.ir

INTRODUCTION

There are several dyes named eosin, and specifically the one most commonly used to counter stain hemalum is Eosin Y (Scheme I). Eosin Y is a pink water soluble acid dye which also displays yellow-green fluorescence. Eosin Y, a heterocyclic dye containing bromine atoms, is used in the fields of dyeing, printing, leather, printing ink and fluorescent pigment, etc. Eosin Y is used in paint and dye industries because of its vivid colour. The effective treatment of this effluent is eco-friendly to aqueous environment. Thus, there is a need for introducing an efficient method for the removal or recovery of eosin generated from industrial waste solutions. Traditional techniques, such as coagulation/flocculation,

Scheme I. Chemical structure of Eosin Y.

membrane separation (ultrafiltration, reverse osmosis) or absorption of activation carbon, are only based on phase transfer mechanism of the pollutant. Biological methods are also ineffective to depolarization of Eosin Y for its stability and complex aromatic structure [1-4]. The toxic nature of the dye is still not quantified much but its high content in living systems is proved to be harmful. Thus, the safe removal of such a dye is the prime aim of our present research and this is accomplished by using novel adsorbents. Conducting electroactive polymers such as poly-aniline (PAni) and polypyrrole (PPy) have attracted a great deal of attention in recent years [5-10]. This class of new polymeric materials can be easily synthesized from both aqueous and non-aqueous solutions. However, polyaniline should be prepared in acidic media. The overall electropolymerization of polypyrrole and polyaniline conducting electroactive

polymers may be shown as Scheme II.

Where A⁻ is the counterion incorporated during polymerization. The charged polymer must contain anion to give charge balance and the formation of the PPy film in the oxidized state requires anion as well as electrons to move through the film. The electro-active nature or the switching properties of PPy and PAni have been utilized as the basis of most proposed applications such as sensors, separation devices, rechargeable batteries and controlled drug release. All other applications of these polymers are based on their electrical conductivity and unique electrochemical properties [11-14]. However, this paper deals with a quite different application of these reactive and functional polymers. Our recent studies have shown that these polymers can effectively remove or uptake the heavy metal ions and dyes from aqueous solutions under simple open circuit conditions [15-18].

In this study, PAni and PPy were synthesized directly on the surface of sawdust via chemical route at room temperature. Coated sawdust by a thin layer of polymers was then used for removal of Eosin Y dye from aqueous solutions. The anion exchange properties of polypyrrole and polyaniline conducting polymers are well established and documented [12-14]. Sawdust, the same as other biomaterials or agricultural wastes is a good adsorbent for adsorption of basic dyes such as methylene blue, malachite green and etc. [19-21]. In this research

(a)

(b)
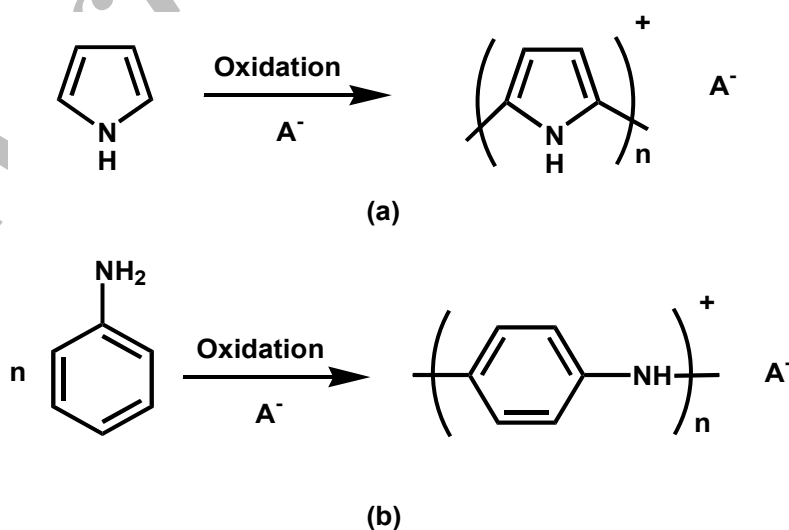
Scheme II. Overall polymerization reactions of: (a) pyrrole and (b) aniline.

sawdust was found to be a very poor adsorbent for adsorption of EY which is an anionic dye and sorption percentage was negligible. Therefore, our research is mainly focused on PPy and PAni coated sawdust for investigation of EY dye removal from aqueous solutions.

Application of polypyrrole and polyaniline conducting polymers doped with releasable or exchangeable counterions for removal of anionic dyes from aqueous solutions based on anion exchange properties of these polymers, introduced in our current study, is a novel research work that can be considered as a highly efficient, cost effective and green way in dye removal technology.

EXPERIMENTAL

Materials and Equipments

All chemicals used were analytical reagent grades and used without further purification. All experiments were carried out in aqueous solutions prepared with de-ionized water. Sawdust (SD), of balsam fir (Abies balsamea) origin was obtained from a local carpentry workshop (Iran). Pyrrole and aniline were purchased from Merck Chemical Company. Monomers were distilled and stored in refrigerator before use. An Eosin Y solution of 100 mg.L^{-1} concentration was prepared in de-ionized water as stock solution. A single beam Perkin-Elmer UV-vis spectrophotometer with 1 cm cell was used for measuring all absorption data. A Metrohm pH meter (model 827) with a combined double junction glass electrode was used for pH determination. The pH adjustments were carried out using dilute NaOH and HCl solutions.

Determination of Eosin Y (EY)

The filtrate dye (EY) concentrations were determined spectrophotometrically at maximum absorption wavelength (515 nm). EY shows an intense absorption peak in the visible region at 515 nm which corresponds to the maximum absorption peak of the EY monomer (Figure 1). A calibration curve for quantitative analysis was obtained at EY dye concentrations range of 0.0-5.0 mg.L^{-1} at pH value of 4, provided by the dye in de-ionized water (Figure 2).

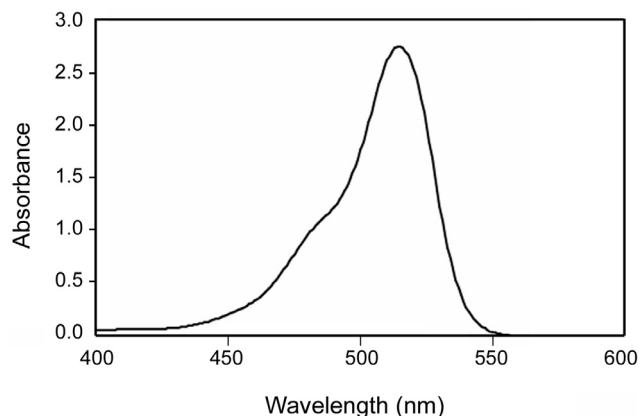**Figure 1.** Visible spectrum obtained for EY (C_o = 30 mg.L^{-1}, pH 4).

Preparation of the Polymer

The polymers were synthesized straight on sawdust surface, which was previously soaked in monomer solutions (0.20 M) by slow addition of chemical oxidants (0.50 M FeCl$_3$ for PPy and 0.20 M (NH$_4$)$_2$S$_2$O$_8$ in HCl 1.2 M for PAni) at room temperature. Sawdust was first washed copiously with distilled water in order to remove any dust or impurities and finally dried at temperature of about 60°C for 2 h in an air circulating oven. In order to have uniform coating and reproducible results, the substrate sawdust sieved (35-50 μ) before coating. Sawdust samples were first soaked in monomer solution for 2 h at room temperature. The mixture was filtered and then the oxidant solution was gently added onto the sawdust. Polymerization was carried out on the surface of sawdust immediately after the addition of oxidant solution. The polymer coated sawdust by each conductive polymer (termed as
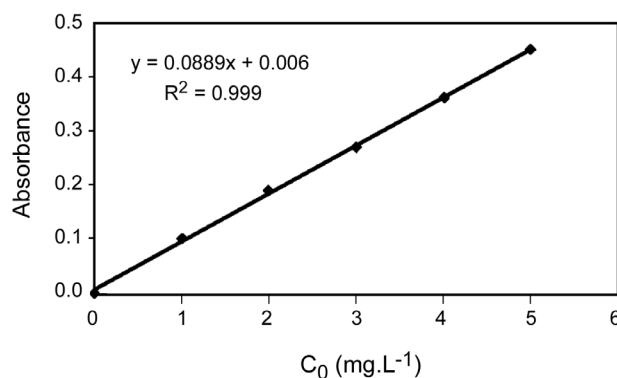

Figure 2. Calibration curve prepared for analysis of EY.

PAni/SD and PPy/SD) was filtered, washed with copious distilled water, dried at about 60°C (in an oven) and sieved before use. Employing 35-50 mesh size particles was a proper choice since higher mesh size particle in spite of having greater surface area and sorption capacity, could not be used in columnar system due to its limited flow rate. The coating percentage of each polymer onto sawdust determined by weight difference of the dried sawdust before and after coating was about ~5%. The details are given in our previously published papers [16,17].

Adsorption Experiments

In batchwise experimental process, a fixed amount of each sorbent was treated with Eosin Y solution (0-100 mg.L^{-1}) at room temperature. During each experiment, the solutions were agitated using a mechanical shaker. In column experiments a glass column with dimensions of 1.0 cm diameter and 15 cm height was employed. One gram sorbent (PPy/SD or PAni/SD) was packed in the column (bed volume ~5 cm^3), and then the EY solution (50 mg.L^{-1}) was passed through the column with flow rate of 3 mL.min^{-1} at room temperature. The outlet solution was analyzed for residual EY solution. The following equations were used to calculate the percentage of sorption and the amount of adsorbed EY solution, respectively:

$$Sorption\ (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \tag{1}$$

$$\frac{X}{m} = \frac{(C_o - C_e)\,V}{m} \tag{2}$$

where C_o and C_e are the initial and equilibrium concentrations of the EY (mg.L^{-1}); X/m is the amount of EY adsorbed onto unit amount of the adsorbent (mg.g^{-1}) at equilibrium; and V is the volume of the solution used in the adsorption experiment (L). Alternatively, regeneration of the used adsorbent was examined. Desorption efficiency was measured using the following equations:

$$Desorption\ (\%) = \frac{m'}{m_o} \times 100 \tag{3}$$

$$m' = C_e \times V' \quad and \quad m_o = (C_o - C_e) \times V \tag{4}$$

where m_o is mg of the sorbent material (EY) onto the adsorbent; m' is mg of EY in the regenerated solution; and V' is the volume of eluent solution (L). C_o and C_e are the respective initial (inlet) and equilibrium (outlet) concentrations (mg.L^{-1}) of EY. In order to obtain accurate and precise data, each experiment was repeated at least three times and the mean values with the maximum relative standard deviation (RSD) less than 1% are reported.

RESULTS AND DISCUSSION

Sorption of EY by PAni/SD and PPy/SD (Batch System)

The effect of some important parameters such as initial concentration, pH, sorbent dosage and contact time on adsorption of EY using the selected adsorbents (PAni/SD and PPy/SD) was investigated as follows.

Effect of pH

The pH of dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. For this investigation, 0.80 g of each portion of PAni/SD and PPy/SD was treated separately with 50 mL of EY solution (50 mg.L^{-1}) at various pH values 2-12 using dilute HCl and NaOH solutions. The variation of EY adsorption on the employed adsorbents over a broad range of pH is shown in Table 1.

The data in Table 1 indicate that the adsorption is higher below pH 8 than its above where the adsorption is dropped. In acidic conditions the surface of the adsorbent is positively charged due to the high concentration of H$^+$, so the electrostatic attraction between the adsorbents (PPy/SD and PAni/SD) and the adsorbate (EY) which is an anionic dye is enhanced. Lower adsorption of EY under alkaline condition, is probably due to the presence of OH$^-$ ions on the surface of adsorbents competing with the adsorbate (anionic dye) for adsorption sites. Since dye EY is precipitated under acidic conditions at pH values lower than 2, all the investigations were carried out at pH about 4 provided by the dye.

As it is shown in Scheme II, PPy and PAni have

Table 1. Effect of pH on sorption or removal percentage of EY by PPy/SD and PAni/SD adsorbents.

pH	2	4	6	8	10	12
Sorption EY by PPy/SD (%)	99.54	99.12	98.70	96.48	95.30	60.21
Sorption EY by PAni/SD (%)	99.60	99.35	98.60	95.51	90.75	55.20

positively fixed charged sites which are balanced with the anions orginating from monomer or oxidant solution during their synthesis. The small size dopant anions can be exchanged with other anionic species in treated solutions which have stronger interactions with the polymer. Removal of EY by the polymers coated onto sawdust is therefore supposed to occur by ion-exchange mechanism as shown in the following chemical equation:

$$2PPy^+/Cl^-(polym) + EY^{2-}(aq) \rightarrow$$

$$(PPy^+)_2 EY^{2-}(polym) + 2Cl^-(aq) \qquad (5)$$
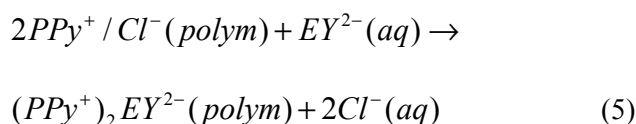
As it is indicated in this equation, during ion-exchange process, mobile Cl^- ions are exchanged with EY anions, and released into solution. Analysis of the solution for chloride ion content after adsorption experiment, by precipitation titration with silver nitrate (Volhard's method), was about twice the mole number of EY before treatment. This analysis interestingly confirms our suggested mechanism as shown by eqn (5). The uptake of each mole of EY dye (divalent charged) can displace two Cl^- ions (monovalent) during incorporation into polymer matrix in order to maintain charge balance. Therefore, it may be concluded that removal of EY dye using PPy/SD or PAni/SD occurs mainly via ion-exchange reaction. However, the importance of other processes such as electrostatic interactions between highly polar and positively charged polymer and negatively charged EY dye molecules and also other intermolecular interactions such as H^- bonding between adsorbent and adsorbate (dye) cannot be ignored.

Effect of Sorbent Dosage

In this test different amounts (0.10-1.0 g) of the selected sorbents were treated with 50 mL EY solution of 50 mg.L^{-1} concentration at optimum pH values (pH 4). The results are shown in Figure 3. It is

apparent that both PAni/SD and PPy/SD adsorbents can remove EY quickly and with increasing sorbent dosage up to 0.80 g, sorption percentage is also increased gradually and then remain constant. This is probably due to the greater availability of the exchangeable sites and surface area.

Effect of Initial Concentration

For performing this experiment, 0.8 g portion of each dried adsorbent was treated with 50 mL of EY solution with concentration of 20-100 mg.L^{-1} at pH 4 for 1 h accompanied by mild shaking at room temperature. The results obtained are summarized in Table 2. As our results indicate, both adsorbents (PPy and PAni coated onto sawdust) showed high performance for adsorption of EY dye within the range of initial concentrations of the dye. The data obtained in this experiment confirm clearly the high performance of the currently introduced adsorbents (PPy and PAni) for removal of anionic dye of EY.

Effect of Contact Time

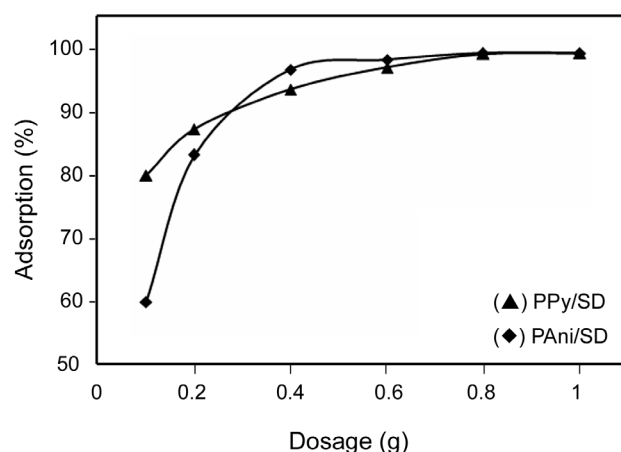For performing this experiment, 0.8 g each adsorbent was treated with 50 mL of 50 mg.L^{-1} EY for different

Figure 3. Effect of adsorbent dosage on removal of EY (m = 0.1-1.0 g, C_o = 50 mg.L^{-1}, time = 60 min, pH 4).

Adsorbent	C_o (mg.L^{-1}) of EY				
	20	40	60	80	100
Sorption (PPy/SD) (%)	99.71±0.62	99.48±0.56	99.02±0.32	98.86±0.40	98.56±0.67
Sorption (PAni/SD) (%)	99.68±0.44	99.52±0.38	99.20±0.51	98.50±0.64	97.90±0.70

time periods (5-60 min) accompanied by stirring at room temperature. The adsorption profiles obtained from the analysis of unabsorbed EY solution are shown in Figure 4. As the results indicate, removal of EY using the selected adsorbents occurs quickly and it is not a highly time-dependent process. It was found that about 95% removal of EY occurs within 20 min. This confirms a high and rapid adsorption of EY dye by PAni and PPy coated sawdust adsorbents.

Adsorption Kinetics

In order to investigate the mechanism of sorption, two kinetic models were tested including Lagergren and pseudo-second-order models [22,23].

Pseudo-first-order Model

For a batch contact time process, where the rate of dye sorption onto a given adsorbent is proportional to the amount of dye sorbed from solution, a pseudo-first-order Lagergren kinetic equation can be expressed as:
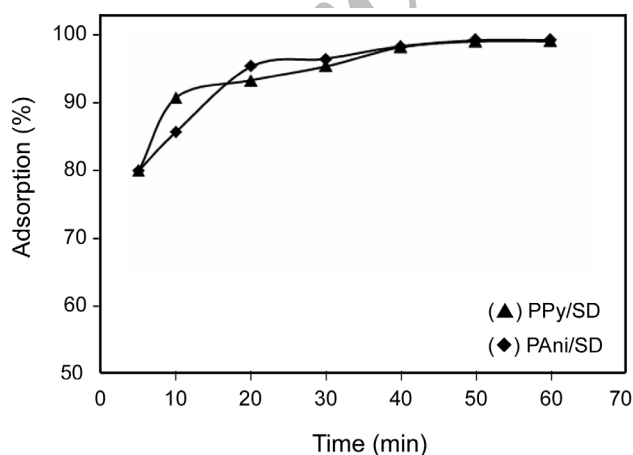
$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

Figure 4. Effect of agitation time on removal of EY (m = 0.8 g, C_o = 50 mg.L^{-1}, time = 5-60 min, pH 4).

where q_t and q_e (mg/g) are the amounts of dye adsorbed per unit mass of the adsorbent at time t and at equilibrium, respectively. The experimental q_e was calculated the same as X/m using eqn (2) and q_t was calculated using the following equation:

$$q_t = \frac{(C_o - C_t)\,V}{m} \tag{7}$$

where C_t (mg/L) is the concentration of dye in liquid phase at time t. A linear plot of $\ln(q_e-q_t)$ versus t, provided the adsorption of first-order kinetics. The equilibrium rate constants of pseudo-first-order adsorption, k_1 (min^{-1}) and the calculated equilibrium sorption capacity, q_e (mg/g), can be obtained from the slope and intercept of the linear plot, respectively.

Pseudo-second-order Model

To describe dye adsorption, a modified pseudo-second-order equation is expressed as follows [20]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{8}$$

where k_2 (g.mg^{-1}.min^{-1}) is the rate constant for pseudo-second-order adsorption model. For the boundary conditions t = 0 to t = 60 min and q_t = 0, $q_t = q_t$ integrated form of equation is as follows:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{9}$$

The linear form of equation can be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^{\,2}} \tag{10}$$

The plots of t/q_t versus t should give straight lines where slopes and intercepts are respectively $1/q_e$ and

Table 3. Comparison of adsorption kinetic parameters for the first- and second-order sorption of EY onto PPy/SD and PAni/SD.

Adsorbent	Pseudo-first-order				Pseudo-second-order			
	$q_{e(exp)}$	k_1	$q_{e(calc)}$	R^2	$q_{e(exp)}$	k_2	$q_{e(calc)}$	R^2
PPy/SD	3.093	0.074	0.781	0.934	3.093	0.235	3.148	0.999
PAni/SD	3.109	0.083	0.880	0.971	3.109	0.198	3.186	0.999

Conditions: m = 0.8 g, C_o = 50 mg.L^{-1}, time = 0-60 min, pH 4. $q_{e(exp)}$ was calculated from our experimental adsorption data at equilibrium using eqn (2). R^2 and $q_{e(calc)}$ for each kinetic model were obtained from their linear plots.

$1/k_2 q_e^2$.

The values of rate constant, k_2, and sorption capacity, q_e, are calculated from these parameters. The results obtained are summarized in Table 3. As our kinetics data show (Table 3), using pseudo-second-order kinetic model, the experimental sorption capacity, $q_{e(exp)}$ values are very close to calculated sorption capacity, $q_{e(calc)}$. The kinetics data and correlation coefficients (R^2) presented in Table 3, interestingly confirm that sorption of EY onto PPy/SD and PAni/SD has followed a pseudo-second-order kinetics model. The pseudo-second order rate expression is based on the sorption capacity of solids and describes chemisorption mechanism for dye removal [24].

Column Studies

Treatment of Data Using Adsorption Isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. Several isotherm equations are available; in the present investigation the equilibrium data were analyzed using the Freundlich and Langmuir isotherms expression [25,26]. The Freundlich equation deals with physico-chemical adsorption on heterogeneous surfaces. Freundlich isotherm (eqn (11)) assumes that the uptake of adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Langmuir model (eqn (12)) assumes that the uptake of adsorbate occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed species. The Freundlich and Langmuir isotherms are expressed as shown by eqns (10) and (11), respectively:

$$Freundlich : \frac{X}{m} = K_f C_e^{\frac{1}{n}} \quad (11)$$

$$Langmuir : \frac{X}{m} = \frac{X_m K_L C_e}{1 + K_L C_e} \quad (12)$$

where K_f (mg.g^{-1}) and n are Freundlich constants related to sorption capacity and sorption intensity of adsorbents. The value of n falling in the range of 1-10 indicates a favourable sorption [27]. In Langmuir model, X/m (mg.g^{-1}) is the adsorption density at equilibrium of EY, C_e is the equilibrium (unadsorbed) concentration of the dye in solution, X_m (mg.g^{-1}) is the monolayer adsorption capacity, and K_L is the Langmuir constant related to the free energy of adsorption. The linearized forms of Freundlich and Langmuir equations can be written as eqns (13) and (14):

$$\log \frac{X}{m} = \log K_f + \frac{1}{n} \log C_e \quad (13)$$

$$\frac{m}{X} = \frac{1}{X_m} + \frac{1}{X_m K_L} \frac{1}{C_e} \quad (14)$$

The values of n and K_f (Freundlich constants) calculated from the slope and intercept of the linear plot of logX/m against logC_e and subsequently the values of K_L and X_m (Langmuir parameters) calculated from the slope and intercept of the linear plot m/X against $1/C_e$ are presented in Table 4. The Freundlich and Langmuir constants and corresponding correlation coefficients for PPy/SD and PAni/SD are given in Table 4. The values for n are 1< n < 3, suggesting that the EY dye adsorption

Table 4. Adsorption isotherm constants for the sorption of EY onto PPy/SD and PAni/SD adsorbents.

Adsorbent	Langmuir isotherm parameters			Freundlich isotherm parameters			
	K_L	X_m	R^2	n	K_F	R^2	R_L
PPy/SD	4.86	5.57	0.9811	2.04	5.10	0.9960	0.002
PAni/SD	4.12	5.90	0.9953	2.25	4.68	0.9781	0.002
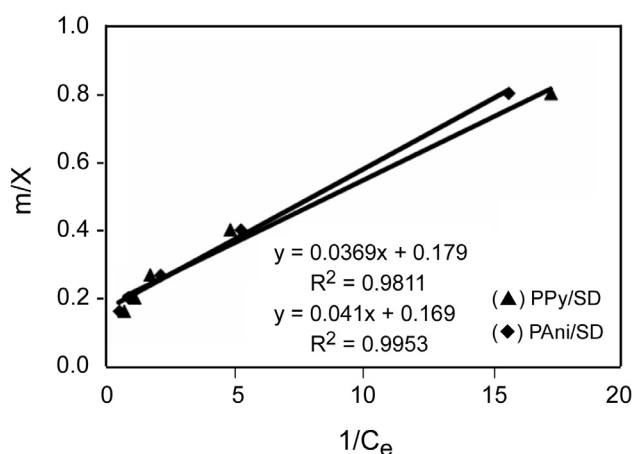
Figure 5. Langmuir isotherm obtained for sorption of EY.

on PPY or PAni is very favourable [28]. The linear plots of both isotherms (Figures 5 and 6) and the derived correlation coefficient values $R^2 > 0.98$ show that the experimental data reasonably well fitted the linearized equations of both Langmuir and Freundlich isotherms. The essential characteristics of the Langmuir isotherm and the favourable nature of
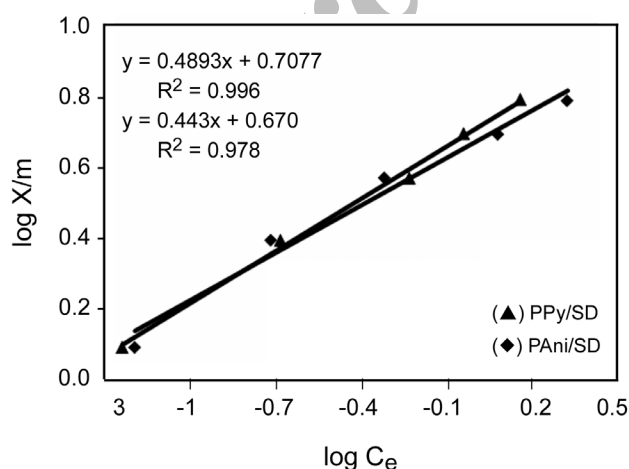
Figure 6. Fruendlich isotherm obtained for sorption of EY.

adsorption can also be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by eqn (15):

$$R_L = \frac{1}{1 + K_L C_o} \tag{15}$$

where K_L (L.mg^{-1}) is the Langmuir constant and C_o is the maximum initial dye concentration in solution (mg.L^{-1}). The values of R_L indicate the type of isotherm as being irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) [25,26]. The calculated value of R_L (0.02) obtained for highest concentration (100 mg.L^{-1}) for both PPy/SD and PAni/SD are indications (Table 4) of both being suitable adsorbents for removal of EY from aqueous solutions with favourable isotherms.

Breakthrough Curves for Removal of EY Using PAni/SD and PPy/SD Adsorbents
Sorption isotherms which are obtained from batch study do not give accurate scale-up data for industrial treatment systems since sorption in a column which is not normally at a state of equilibrium. Consequently, there is a need to perform flow tests using columns to evaluate the performance of adsorbent. The design of packed bed adsorbent in continuous systems, concentration versus time or volume of solution usually yields an *S*-shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a "breakthrough curve". The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion.

For performing this experiment, 1.0 g PAni/SD and PPy/SD packed in a glass column (fixed bed depth of 5 cm^3), and then EY solution with concentration of 50 mg.L^{-1} passed through the
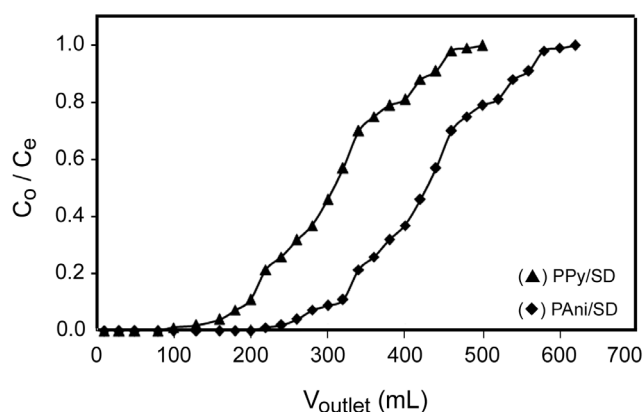
Figure 7. Breakthrough curves for removal of EY (m = 1.0 g, C_o = 50 mg.L^{-1}, pH 4, flow rate = 3 mL.min^{-1}).

column with constant flow rate (3 mL.min^{-1}) at pH 4.0. Each time 10 mL was poured into the column. The outlet solution was analyzed for unabsorbed EY solution in order to obtain the "breakthrough curve", which Figure 7 depicts the sorptions of EY obtained for PAni/SD and PPy/SD used in a column system.

Desorption Studies (Using Column System)
Desorption studies help to elucidate the nature of adsorption and the possibility of recycling the used adsorbent and adsorbate. In order to commercialize an adsorption system, the recovery of the adsorbent or adsorbate is very important. A favourable adsorption system not only should have high regeneration efficiency but to be also cost effective. The choice of NaCl and HCl chemicals was based on use of chloride ions as dopant for desorbing the EY anions. PAni is transformed into emeraldine base form (non-ionic) under alkaline conditions [30], so it is assumed that the adsorbed EY dyes to be released from the polymer through ion-exchange or electrostatic interactions after alkaline treatment. Hydroxide ions can also compete with the anionic adsorbate for adsorption onto an adsorbent since the negatively charged

surface of an adsorbent leads to desorption because of electrostatic or columbic repulsions.

For performing this experiment, 1.0 g of adsorbents PAni/SD and PPy/SD was first treated with 50 mL of EY solution of 50 mg.L^{-1} initial concentration at pH value of 4. To test the regeneration of the adsorbent, distilled water, NaCl (1 M), dilute HCl (0.1 M) and NaOH (0.05 M) solutions were used as the desorbing agents. The results obtained are depicted in Table 5.

As our data indicate, dilute NaOH (0.05 M) was able to desorb the adsorbed dyes to the greatest extent. The analysis of the filtrate solution (using eqns (3) and (4)) for the released dye showed that more than 99% of sorbed EY has been removed from the PPy/SD column. It might be possible to improve desorption efficiency using more concentrated alkaline solution, since sawdust (as substrate) and PPy are not very chemically stable under strong mineral alkaline or acidic conditions. Therefore, application of stronger NaOH or HCl solution for recovery of the column was avoided. Desorption of EY dye from PPy/SD or PAni/SD using alkaline solution may imply physisorption mechanism of the EY molecules through ion-exchange process onto adsorbents.

CONCLUSION

Polyaniline and polypyrrole conducting polymers can be easily synthesized via chemical oxidation directly on the surface of sawdust from aqueous solutions. Sawdust is a widely abundant and environmentaly friendly natural material to be used as substrate. It is a proper choice for coating conducting/electroactive polymers in order to be used for adsorption of dyes from aqueous solutions. EY dye removal by the PPy and PAni is supposed to occur mainly via

Table 5. Effect of different chemicals used for desorption percentage of EY.

Adsorbent	Regenerant solution			
	Distilled water	NaOH (0.05 M)	HCl (0.1 M)	NaCl (1 M)
PAni/SD	0	52%	0	0
PPy/SD	0	96%	0	25%

anion-exchange process. In the case of PPy/SD above 96% of EY dye can be recovered using 0.05 M NaOH as regenerant solution at room temperature. Regeneration of the adsorbent (PPy/SD) or recovery of the adsorbate (EY dye) is possible with high performance which makes it possible for frequent use. The currently introduced adsorption systems (PAni/SD and PPy/SD) seem both very economical and efficient for removal of acid dyes such as EY from aqueous solutions. The findings in this paper seem to be very important from application point of view for water and wastewater treatments in dye removal technology.

ACKNOWLEDGEMENT

SYMBOLS AND ABBREVIATIONS

C_t Concentration at time t (mg/L)
C_o Initial concentration (mg/L)
C_e Equilibrium concentration (mg/L)
X/m   Amount of dye adsorbed onto unit amount of the adsorbent (mg/g)
V   Volume of the solution (L)
m_o Milligram of the sorbed material onto the adsorbent (mg)
m' Milligram of EY in the regenerated solution (mg)
V' Volume of eluent solution (L)
q_t Amount of dye adsorbed per unit mass of the adsorbent at time t (mg/g)
q_e Amount of dye adsorbed per unit mass of the adsorbent at equilibrium (mg/g)
t   Adsorption time (min)
k_1 Equilibrium rate constant of pseudo-first-order adsorption (min^{-1})
k_2 Equilibrium rate constant of pseudo-second-order adsorption (g/mg.min)
X_m Maximum amount sorbed (mg/g)
b   Langmuir's constant (L/mg)
K   Freundlich's constant (mg/g)
n   Freundlich's constant
R_L A dimensionless equilibrium parameter for express of Langmuir's equation
SD   Sawdust without coating
PPy/SD Polypyrrole coated onto sawdust
PAni/SD Polyaniline coated onto sawdust
EY   Eosin Y

REFERENCES

1. Kositzi M, Antoniadis A, Poulios I, Kiridis I, Malato S, Solar photocatalytic treatment of simulated dyestuff effluents, *Sol Energy*, **77**, 591-600, 2004.
2. Pérez M, Torrades F, Doménech X, Peral J, Fenton and photo-Fenton oxidation of textile effluents, *Water Res*, **36**, 2703-2710, 2002.
3. Xie Y, Chen F, He J, Jincai Z, Wang H, Photoassisted degradation of dyes in the presence of Fe_3^+ and H_2O_2 under visible irradiation, *Photochem Photobiol J*, **136**, 235-240, 2000.
4. Lucas MS, Peres JA, Decolorization of the azo dye reactive black 5 by Fenton and photo-Fenton oxidation, *Dyes Pigments*, **71**, 235-243, 2006.
5. Skotheim TA, Elsenbaumer RL, Reynolds JR, *Handbook of Conducting Polymers*, 2nd ed, Marcel & Dekker, New York, 1998.
6. Mirmohseni A, Oladegaragoze A, Farbodi M, Synthesis and characterization of processable conducting polyaniline/polystyrene composite, *Iran Polym J*, **17**, 135-140, 2008.
7. Zeng XR, Ko TM, Structures and properties of chemically reduced polyanilines, *Polymer*, **39**, 1187-1195, 1998.
8. Gospondinova N, Terlemezyan L, Polyaniline conducting polymers prepared by oxidative polymerization, *J Prog Polym Sci*, **23**, 1443-1484, 1998.
9. Kang ET, Neoh KG, Tan KL, Polyaniline: a polymer with many interesting intrinsic redox states, *J Prog Polym Sci*, **23**, 277-324, 1998.
10. Huang WS, Humphrey BD, MacDiarmid AG, Polyaniline, a novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes, *J Chem Soc Faraday Trans*, **82**, 2385-2400, 1986.
11. Miras MC, Acevedo DF, Monge N, Frontera E,

Rivarola CR, Barbero CA, Organic chemistry of polyanilines: tailoring properties to technological applications, *J Open Macromol*, **1**, 58-73, 2008.

12. Parsa A, Hosseini SH, Asefoddoleh M, Anion exchange properties and kinetic behavior of polyaniline-coated silica GEL for anion phosphates, *Eur J Sci Res*, **26**, 369-375, 2009.

13. Ansari R, Price WE, Wallace GG, Quartz crystal microbalance studies of the effect of solution temperature on the ion-exchange properties of polypyrrole conducting electroactive polymers, *React Funct Polym*, **56**, 141-146 , 2003.

14. Hosseini SH, Noor P, Ion exchange properties and kinetic behavior of polyaniline-coated silica gel for *p*-toluenesulphonic acid and methane-sulphonic acid, *Iran Polym J*, **14**, 55-60, 2005.

15. Ansari R, Raofie F, Removal of mercuric ion from aqueous solutions using sawdust coated by polyaniline, *E-J Chem*, **3**, 35-43, 2006.

16. Ansari R, Application of polyaniline and its composites with conventional polymers for adsorption/recovery of chromium hexavalent from aqueous solutions, *Acta Chim Slov*, **53**, 88-94, 2006.

17. Ansari R, Fahim NK, Application of polypyrrole coated on wood sawdust for removal of Cr(VI) ion from aqueous solutions, *React Funct Polym*, **67**, 374-367, 2007.

18. Ansari R, Dellavar AF, Removal of silver ion from aqueous solutions using conducting/electroactive polymers, *J Iran Chem Soc*, **5**, 657-668, 2008.

19. Ahmad A, Rafatullah M, Sulaiman O, Ibrahim MH, Hashim R, Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution, *J Hazard Mater*, **170**, 357-365, 2009.

20. Wang XS, Zhou Y, Jiang Y, Sun C, The removal of basic dyes from aqueous solutions using agricultural by-products, *J Hazard Mater*, **157**, 374-385, 2008.

21. Ansari R, Zanjanchi MA, Mohammadkhah A, Mosayebzadeh Z, Removal of basic dyes from textile wastewaters using sawdust, *1st Int 7th National Conf Textile Eng*, Rasht, Iran, 27-29 Oct 2009.

22. Ho YS, Citation review of Lagergren kinetic rate equation on adsorption reactions, *Scientometrics*, **59**, 171-177, 2004.

23. Ho YS, Chiang CC, Sorption studies of acid dye by mixed sorbents, *Adsorption*, **7**, 139-147, 2001.

24. McKay G, Ho YS, Pseudo-second-order model for sorption processes, *Process Biochem*, **34**, 451-465, 1999.

25. Debelak KA, Schrodt JT, Comparison of pore structure in Kentucky coals by mercury penetration and carbon dioxide adsorption, *Fuel J*, **58**, 732-736, 1979.

26. Freundlich U, Die adsorption in lusungen, *J Phys Chem*, **57**, 385-470, 1906.

27. Noroozi B, Soria GA, Bahrami H, Arami M, Equilibrium and kinetic adsorption study of a cationic dye by a natural adsorbent-silkworm pupa, *J Hazard Mater*, **139**, 167-174, 2007.

28. Kadirvelu K, Thamaraiselvi K, Namasivayam C, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, *Sep Purif Technol*, **24**, 497-505, 2001.

29. Sujatha M, Geetha A, Sivakumar P, Palanisamy PN, Orthophosphoric acid activated babul seed carbon as an adsorbent for the removal of methylene blue, *J Chem*, **5**, 742-753, 2008.

30. Ikkala OT, Laakso J, Counter-ion induced processibility of polyaniline: conducting melt processible polymer blends, *Synth Met*, **69**, 97-105, 1995.