ION EXCHANGE LETTERS

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Ion Exchange Letters **3** (2010) 19-24

Removal of chromium complex dye from aqueous solutions using strongly basic and weakly basic anion exchangers

Danutė Kaušpėdienė, Eglė Kazlauskienė and Aušra Selskienė

Institute of Chemistry, A.Goštauto 9, 01108, Vilnius, Lithuania, dana@ktl.mii.lt

Received 12.4.2010; Accepted 9.7.2010; Published 24.8.2010

ABSTRACT

Removal of chromium complex dye from aqueous solutions by sorption onto a weakly basic, acrylic matrix anion exchanger Purolite A845 and a strongly basic, polystyrene matrix anion exchanger Purolite A 500P has been investigated under various experimental conditions: the initial dye concentration, pH and temperature. The sorption of chromium complex dye proceeds as a result of miscellaneous interactions between the dye and anion exchanger: ion exchange and physical sorption. The removal efficiency of chromium complex dye was found to be somewhat higher using Purolite A 845 than that using Purolite A 500P in both acidic and neutral solutions. The experimental data are in good agreement with the Langmuir isotherm and the pseudo-second order rate models. The performance of Purolite A 845 in chromium complex dye removal was verified in column experiment. The working capacity was 17,26 mg per gram of dry anion exchanger at the c_0 = 83,4 mg/L and pH 2. The maximum concentration of dye in eluate was obtained using a 2-3 bed volume mixture (1:1) of 5% NaOH – ethanol.

Keywords: chromium complex dye; sorption; anion exchanger

INTRODUCTION

The textile industry is one of the largest fresh water consumers and the producer of diluted, highly colored, complex and variable in nature wastewaters. Dyes are normally present in textile wastewaters at a concentration of 10-50 mg/L; however, the color can be observed above 1 mg/L[1]. The presence of dyes in waters makes them not only aesthetically objectionable but also causes many environmental problems[1,2].

Metal complex dyes are a problematic group of substances, present in the negatively charged anion form in mixed wastewater from textile, tanning industries that should be removed[3-5]. Environmental concerns arise from the carcinogenic properties of metals (Cr, Co, Cu), from amines formed by reductive cleavage of azo groups of organics and color[2,5]. Therefore, a complete removal of these hazardous dyes from wastewaters is necessary to prevent them from release into the environment.

From the practical point of view the dye and other impurities from wastewater can be removed to the requirements for reuse it as process water. The sorption is often one the most effective methods for the dye removal from diluted solutions among several chemical and physical methods. The removal of various textile and food dyes using different anion exchangers (strongly and weakly basic) of gel or macroporous structures of styrene-divinylbenzene or acrylic matrices was studied [6-11]. There is very little information in literature on the removal of metal complex dyes using anion exchangers[6]. Because removal of dyes is based on dye – anion exchanger interaction that depends on the number and type of functional groups or the chemical and physical structures of matrix and on the structure of dye, the related performance of anion exchanger should be evaluated in the particular case[6,12]. As the total capacity cannot be readily determined, it is necessary to carry out experimental study under the determined conditions.

In this paper, therefore, we aimed at investigating the removal from aqueous solutions of textile, chromium complex dye (Lanasyn Navy M-DNL) by weakly and strongly basic anion exchange resins Purolite A 845 and Purolite A 500P. The effects of initial dye concentrations, contact time, solution pH as well as temperature on dye adsorption in batch experiments were investigated. Special attention was given to the variation in removal of hazardous components such as chromium and organic substances (COD). The performance of Purolite A 845 in dye removal was examined in column experiment.

EXPERIMENTAL

The tested chromium complex dye was the non biodegradable, commercial textile dye anionic Lanasyn Navy M-DNL (1:2 chromium monoazo complex (trisodium bis[3-hydroxy-[(2-hydroxy-1-naphthyl)azo]naphthalene-1-sulphonato(3-)]chromate(3-)) (Fig. 1). It was obtained from Clariant Product AG. The concentration of dye solution in the series ranged from 30 to 616 mg/L. The pH values of initial solutions were measured and adjusted with 0.1 M HCl.

Sorption experiments were observed on two types of anion exchangers obtained from Purolite International Ltd.: 1) gel, polyacrylic – divinylbenzene, weakly basic (functional groups – $N(CH_3)_2$, *total capacity 1,6 eq/L*) Purolite A845 and 2) macroporous, styrene-divinylbenzene, strongly basic, type I (functional groups – $N(CH_3)_3$, *total capacity 0,8 eq/L*) Purolite A 500P. Purolite A 845 is recommended for demineralization of water high in organic matter, whereas Purolite A 500P – as an organics scavenger from industrial and domestic water supplies.

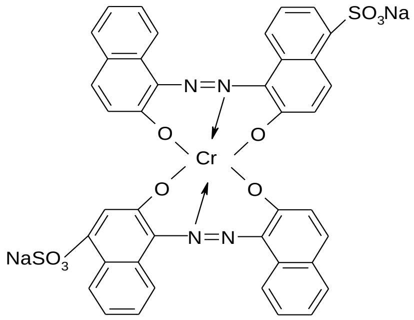


FIGURE 1 *Chemical structure of dye Lanasyn Navy M-DNL*

Experiments were carried out in the batch by mixing 0,5 g of anion exchanger in OH^- form with 25 ml of a given initial concentration aqueous dye solution for 5 – 360 min. At the end of the predetermined time interval, the anion exchanger was removed by centrifugation and the residual concentration of dye ascertained by UV-Vis Spectrometer Cintra 101 (GBS Scientific Equipment (USA) LLS) at the respective λ_{max} value, which is 616 nm for this dye. The dye concentration was calculated from calibration curve.

The data obtained from sorption experiments were used to calculate the dye removal R [%], equilibrium constant K_c, sorption capacity of anion exchanger q_t at phase contact time t, and q_e [mg/g] at phase contact time for attainment of equilibrium:

$$R = \frac{c_0 - c_e}{c_0} \times 100 \quad (1)$$

$$K_c = \frac{c_0 - c_e}{c_e} \quad (2)$$

$$q_{t(e)} = \frac{\left(c_0 - c_{t(e)}\right)V}{m} \quad (3)$$

where c_0 and c_t are the concentrations [mg/L] of the dye in the solution before and after sorption, respectively, c_e is the concentration of dye at equilibrium [mg/L], V is the volume of the solution [ml] and m is the mass of the dry anion exchanger [g].

Kinetic values of adsorption were determined by analyzing adsorptive uptake of the dye used from 33,36 mg/L dye solution at initial pH 2 at different time intervals at temperatures of 293 – 333 K.

The column experiments were performed in order to measure of sorption / desorption curves in the one-centimeter diameter column filled with 6,3 mL swollen anion exchanger. Then dye solution of the initial concentration 83,4 mg/L and pH 2 was passed through the anion exchanger bed at the volume velocity of 1mL/cm^2 min. The dye desorption (regeneration of anion exchange capacity) was applied with dye saturated anion exchanger using mixture 1:1 of 5% NaOH - ethanol and keeping volume velocity of 0,5 mL/cm^2 min. The effluent was collected in the fractions and the dye concentration was determined.

The chemical oxygen demand (*COD*) values of the dye solutions were determined using a Spectroquant TR 320 – Spectroquant Picco analyser.

The concentration of chromium was determined using ICP optical emission spectrometry (Optima 7000DV, Perkin Elmer).

RESULTS AND DISCUSSION

The effects of the initial dye solution pH (pH 2,0 – 7,5) on the removal of dye at 293 K are shown in Fig. 2. The dye removal for both anion exchangers investigated were much higher in acidic than in neutral solutions. The maximum dye removal occurred at the initial pH 2 for both weakly basic and strongly basic anion exchangers. Therefore, the adsorption isotherms and kinetic curves were further measured at the initial solution pH 2.

In aqueous solutions, the dye was dissolved[13] and the strongly sulfonate group of the chromium complex dye was dissociated and converted to anionic dye ions – $R^{'}(SO_3)_2^{2-}$.

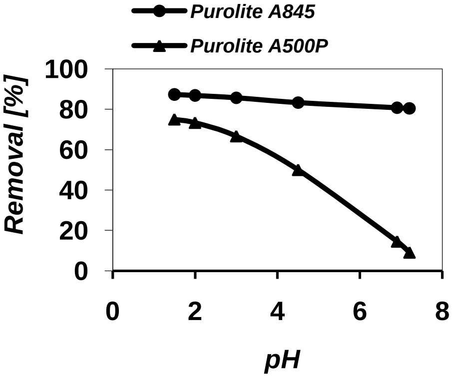


FIGURE 2 *The removal of dye by the Purolite A 845 and Purolite A 500P as a function of pH. The initial dye concentration 33,36 mg/L*

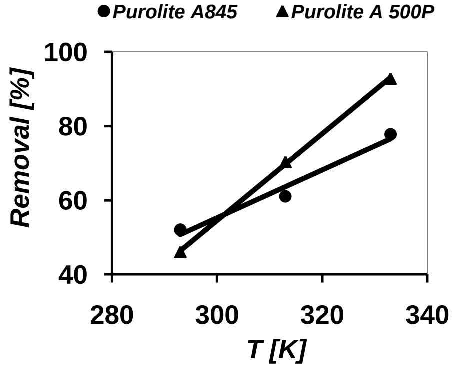


FIGURE 3 *The removal of dye by the Purolite A 845 and Purolite A 500P as a function of temperature. The initial dye concentration 33,36 mg/L at pH 2*

The sorption proceeded due to the formation a stable ion pair ($R_2(SO_3)_2R^{'}$) between the anion of dye ($R^{'}(SO_3)_2^{2-}$) and the functional groups of anion exchanger in OH^- form (ROH). The aromatic ring (styrene, divinylbenzene) in Purolite A 500P, aromatic ring (divinylbenzene) and -C=O groups in Purolite A 845 and groups $–SO_3Na$, -N=N-, aromatic rings in the dye structure can also participate in covalent, coloumbic, hydrogen or weak van der Waals forces. The physical sorption and π-π dispersion forces can also result from the aromatic nature of the anion exchanger and chromium complex dye[10]. So, the amount of the sorbed dye is the summation of sorption on all sites. The following observation confirms the effect of temperature on the removal of dye on anion exchangers (Fig. 3). Removal of dye increased with temperature for both resins which suggested miscellaneous interactions between dye and anion exchanger[10,14,15]. In a conventional model of physical sorption the increase in temperature usually leads to an increase in the rate of the equilibrium attainment, but it decreases the equilibrium capacity[13]. In processes where only ion exchange is involved, the temperature effect on retention time is relatively low[16].

The effect of dye solution concentrations is shown in Fig. 4. The anion exchangers investigated effectively remove the dye at low initial concentrations; at higher concentrations the isotherms reach a maximum capacity as indicated by the plateau of the data. The shape of the experimental isotherms (Fig. 4) indicates L2-behavior accordingly to Giles and Smith classification[17] and is usually associated with ionic solute adsorption (e.g., metal cations and ionic dyes) at weak competition with the solvent molecules. Experimental data fitted to Langmuir isotherm model linearized the equation[18]:

$$\frac{1}{q_e} = (\frac{1}{q_m K_L}) \times \frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

where: q_m [mg/g] the amount of dye adsorbed at complete monolayer coverage; K_L [L/mg] the affinity parameter. The values of K_L and q_m are evaluated from the slope and intercept of the plot of $1/q_e$ *vs* $1/C_e$.The correlation of dye adsorption data with Langmuir isotherm model was high, with R^2 values for Purolite A 845 as Purolite A 500P of 0,9613 and 0,9317, respectively.

The monolayer equilibrium capacitiy q_m obtained for Purolite A 845 [1,12 mg/g] are higher when compared to q_m obtained for Purolite A 500P [0,91 mg/g]. However, these values are lower than those obtained for other anion exchangers[6-12].

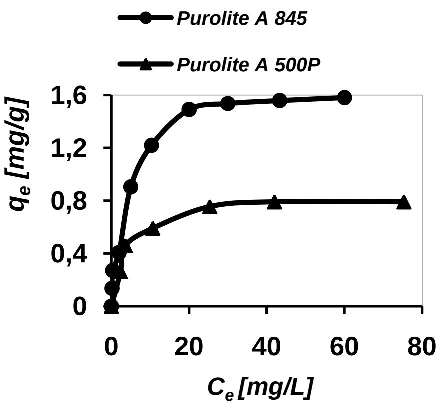


FIGURE 4 *Experimental isotherms for chromium complex dye sorption on Purolite A 845 and Purolite A 500P*

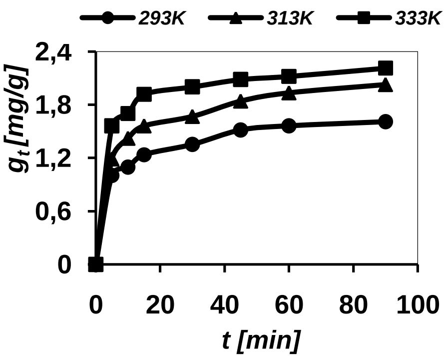
The comparison of the equilibrium adsorption constant value K_L for Purolite A 845 [0,848 L/mg] with that for Purolite A 500P [0,195 L/mg] suggests that a weakly basic anion exchanger is fourfold favorable for the adsorption of dye than a strongly basic anion exchanger. However, a direct comparison of the data obtained in this work with those in literature is not possible since different sorbents and dyes were used, besides that dye and experimental conditions are not the same.

The chemical reactions such as chemisorption, physical sorption, ion exchange, or complexation[17] can affect sorption kinetics as profoundly as they affect the equilibrium. The pseudo-second-order model was selected because there is no need to know the equilibrium capacity from the experiments, as it can be calculated from the mode. The rate constant of sorption was determined using the pseudo-second order equation[19,20] in the linear form:

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

where k_2 is the pseudo-second order rate constant [g/(μmol min]. The plot of t/q_t *vs* t shows a linear relationship for Purolite A 845 and Purolite A 500P. q_e and k_2 values were determined from the slop and intercept of the plot, respectively and are given in Table 1. The correlation coefficients (R^2) are high, in the range of 0.9915 – 0.9984, confirming a good agreement with the experimental data. The rate constants, k_2, for chromium complex dye sorption on Purolite A 845 with an increase in the solution temperature from 293 K to 313K indicate a slight decrease from 0,1608 to 0,1217 g/ [mg min] and an increase from 0,1217 to 0,1964 g/[mg min], with temperature increase from 313 K to 333 K. A variation of k_2, for Purolite A 845 indicates that the adsorption mechanism at a higher temperature is different from that at a lower temperature. Whereas k_2 values obtained for Purolite A 500P sharply decrease with increase in temperature from 293K to 333K. The values of q_e increase with temperature of dye adsorption on both Purolite A 845 and Purolite A 500P (Table 1).

A) ***Purolite A845:***



B) ***Purolite A500P:***

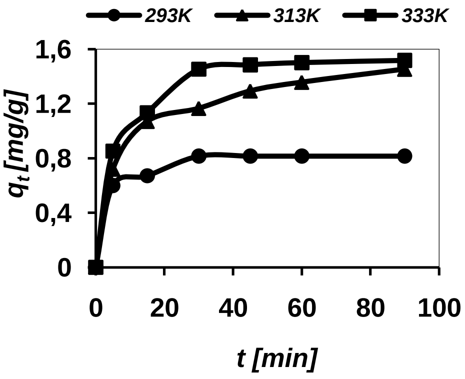


FIGURE 5 *Kinetic curves for chromium complex dye sorption on anion exchanger Purolite A845 (A) and Purolite A 500P (B)*

TABLE 1 *Pseudo-second-order rate constants (k_2) and equilibrium sorption values (q_e) for chromium complex dye sorption on Purolite A 845 and Purolite A 500P obtained at various temperatures*

Anion exchanger	**T** [K]	k_2 [g/mg min]	q_e [mg/g]	R^2
Purolite A845	293	0,1608	1,65	0,9959
	313	0,1217	2,07	0,9950
	333	0,1964	2,23	0,9984
Purolite A500P	293	0,8202	0,82	0,9862
	313	0,3038	1,39	0,9915
	333	0,2400	1,57	0,9933

The fact that the sorption of chromium complex dye depends on temperature also indicates that the mobility of the dye molecule increases with increase in temperature [10]. Consequently it may be concluded that the chromium complex dye adsorption mechanism onto both the anion exchangers investigated consists of ion exchange, physical sorption and diffusion. On one hand, the sorption does not follow exclusively the physical sorption mechanism, when generally the rate of approach to equilibrium increases with increase in temperature and the equilibrium adsorption capacity decreases, and, on other hand, the fact that the dye sorption capacity increases with temperature indicates the occurrence of other processes including diffusion[21].

From the kinetic parameters k_2 at different temperatures, the activation energies, representing the minimum energy that the dye-anion exchanger system should have for the reaction of adsorption to proceed, was estimated using Arrhenius relationship[21]:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{6}$$

where E_a is the Arrhenius activation energy of adsorption, *A* the Arrenius factor, *R* the gas constant equal to 8.314 J/mol K, and *T* is the solution temperature. When lnk_2 is plotted against *1/T*, a straight line with a slope $-E_a/R$ is obtained (not presented).

TABLE 2 *Indexes of dye solutions treated using Purolite A 845. Initial solution pH 2, contact time 1 h and temperature 20^{0}C.*

Dye solution before treatment			**Dye solution treated using Purolite A 845**			
c_0 [mg/L]	**Cr** [mg/L]	**COD** [mgO$_2$/l]	*c* [mg/L]	**pH**	**Cr** [mg/L]	**COD** [mgO$_2$/l]
31	0,62	73,5	1,5	2,7	0,03	17
61,5	1,23	147	2,5	2,9	0,05	30
154	3,08	367,5	5	3,1	0,1	50
308	6,16	735	6	3,2	0,12	65
616	12,32	1102,5	12,5	3,4	0,25	140

The positive values of activation energies obtained for anion exchangers Purolite A 845 and Purolite A 500P (9040,56 and 7789,56 kJ/g, respectively), confirms that adsorption is a combination of physico-chemical and ion exchange processes[21].

The variations in removal of hazardous components such as chromium and organic substances, including azo compounds (chemical oxygen demand (COD) at various pH and initial concentrations) using Purolite A 845 are shown in Table 2. It is evident that at the initial pH 2 maximum removals of chromium (residual concentration lower than 0,1 mg/L[22]) and organics (values of chemical oxygen demand lower than 100 mgO$_2$/L[22]) is observed, when the initial concentrations of chromium and organic compounds were lower than 6.16 mg/L and 735 mgO$_2$/l, respectively.

The performance of Purolite A 845 in chromium complex dye removal in column is presented in Fig. 6 and Fig. 7. From the breakthrough curve, presented in Fig. 6, calculated working capacity when dye concentration in effluent reached 0,5 c_0 was 6,56 mg of dye per mL of swollen anion exchanger (17,26 mg per gram of dry anion exchanger). A higher capacity of column operations as compared to in batch experiments was established by a continuously large concentration gradient at the interface zone as it passed through the column, while the concentration gradient decreased with time in the batch experiment.

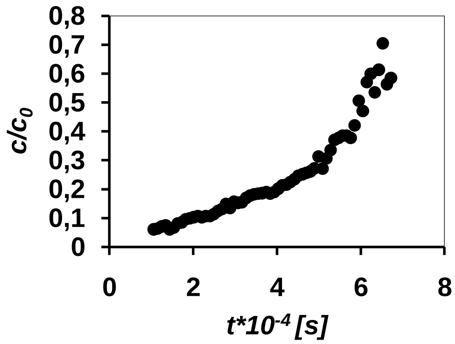


FIGURE 6 *The breakthrough curve of dye sorption onto Purolite A 845.*

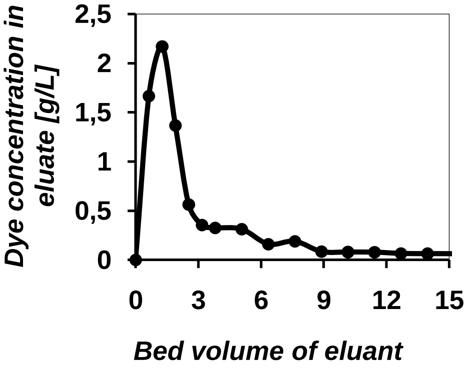


FIGURE 7 *The dye desorption from Purolite A 845 using mixture (1:1) 5% NaOH and ethanol (1:1)*

The maximum concentration of dye in eluate was obtained using a 2-3 bed volume mixture (1:1) of 5% NaOH – ethanol (Fig. 7).

CONCLUSIONS

The degree of chromium complex dye removal from aqueous solutions using weakly basic Purolite A 845 and strongly basic Purolite A 500P anion exchangers depends on the initial dye solution concentration, pH and temperature.

A weakly basic Purolite A 845 anion exchanger exhibits better chromium complex dye sorption equilibrium and kinetic characteristics than a strongly basic Purolite A 500P anion exchanger.

The positive values of activation energies and equilibrium constants increased with temperature for both anion exchangers that suggested the miscellaneous interactions between the dye and anion exchanger: ion exchange and physical sorption.

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