Sunset Yellow sorption on weak base anion exchanger — kinetic and equilibrium studies

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The sorption equilibrium and kinetics of Sunset Yellow dye in aqueous solutions on the weak base anion exchange resin — Amberlite FPA51 were examined in this paper. The influences of phase contact time, solution pH, initial dye concentration and temperature were studied by the batch method. The amounts of dye sorbed at equilibrium changed from 9.9 to 48.7 mg/g with the increasing initial concentrations in the range 100–500 mg/L. The experimental data were analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models of adsorption. The maximum monolayer capacity was 130.6 mg/g. The sorption free energy was equal to 14.6 kJ/mol and revealed the nature of the ion exchange mechanism in this system. The kinetic data were modelled using the pseudo-first order, pseudo-second order and intraparticle diffusion equations.

Keywords and phrases: dye, anion exchanger, adsorption, kinetics.

Introduction

Coloured wastewater is a consequence of batch processes both in the dye manufacturing and dye-consuming industries [1]. Dyes removal, in particular, has recently become an area of major scientific interest. During the past two decades several decolourization techniques have been reported in literature [1, 2]. In general, dyes containing wastewaters can be treated in two ways: (i) by chemical or physical methods and (ii) by means of biodegradation. Physical ones include different precipitation methods (coagulation, flocculation, sedimentation), adsorption (on silica gel, sludge, activated carbon), filtration, reverse osmosis, etc. Biological treatment differs according to the presence or absence of oxygen — aerobic and anaerobic processes. Chemical methods are those, in which chemicals are used for decolourization, and include reduction, ozonation, ion exchange and neutralization [3]. Currently, the major methods of coloured wastewaters treatment involve physical and/or chemical processes. Water soluble dyes such as reactive and acid dyes are not easily removed in conventional biological treatment because of their high solubility and non-biodegrability. The advantages and limitations of various treatment methodologies are reported in many papers, e.g. [1, 2, 4].

It can be concluded that some of these techniques are effective, although they have restrictions such as excess amount of reagents, or accumulation of concentrated sludge with serious disposal problems, expensive plant requirements or large operation costs as well as the lack of effective colour reduction [4]. Adsorption has been known to be one of the most widely employed methods by virtue of its easy operation, ability of removal of various compounds (both organic and inorganic) and simplicity [5]. According to our knowledge, there are still very few comprehensive studies available in literature on dyes removal using anion exchangers. Karcher et al. [6], Wawrzkiewicz and Hubicki [7], Dragan et al. [8] and Dulman et al. [9] proved that functionalized resins exhibit high capacities towards dyes such as Reactive Red 120, Reactive Red 198, Reactive Black 5, Tartrazine, Indigo Carmine, Tiron, Ponceau 4R or Acid Green 9.

The aim of this paper was, therefore, to apply the commercially available macroporous anion exchanger of $-NR2$ functional groups for removal of Sunset Yellow FCF (SY) from aqueous solution. Sunset Yellow is the best known and one of the most commonly used food additives. It is found in the food stuffs, soaps, hair products, moisturizers, crayons, vitamins and medicinal capsules. The sorption capacities of the anion exchanger for Sunset Yellow were investigated by determining the

equilibrium isotherms. Kinetic studies were carried out taking into account the initial dye concentration. The effects of phase contact time, temperature and pH on the dye sorption were also examined.

Experimental

Dye and anion exchange resin

Sunset Yellow FCF known as Food Yellow 3 (FD & C Yellow No.6, C.I. 15985, disodium 6-hydroxy-5-[(4--sulfophenyl)azo]-2-naphthalenesulfononate) is a synthetic azo dye. It is orange to red powder, soluble in water, decomposes at the melting point 360°C. The dye (purity ~90%) was purchased from Sigma-Aldrich (Germany). The stock solution of the dye was prepared by dissolving the accurately weighed amount of dye in 1 L of distilled water. All working solutions were prepared by diluting the stock solution with distilled water. The dye concentrations were measured using a double beam UV-VIS spectrophotometer Specord M42 (Carl Zeiss Jena, Germany) at the maximum absorbance wavelength (481 nm).

Amberlite FPA51 (Rohm and Haas, France) is the macroreticular, weakly basic anionic exchange resin containing tertiary amine functionality on the cross linked polystyrene matrix. The resin was washed with 1 M HCl as well as distilled water in order to remove impurities. Dried resin was used for further experimental studies.

Equilibrium and kinetic studies

Equilibrium and kinetic experiments were carried out using the batch method. 0.25 g of the anion-exchanger and 0.025 L of dye solution (100–1500 mg/L, pH~4.87) were placed in 0.1 L conical flasks. The flasks were shaken in the thermostatic shaker (Elphin 358 S, Ta Poland) with a constant speed of 170 cpm at 20°C for 1–360 min. The amount of dye adsorbed at equilibrium, q_e (mg/g) was calculated from Eq. (1):

$$q_e = \frac{(C_0 - C_e)}{w} \times V \tag{1}$$

where: C_0 — initial concentration of dye (mg/L),
    C_e — concentrations of dye in the solution at equilibrium (mg/L),
    V — volume of the solution (L),
    w — mass of the dry anion-exchanger (g).

Taking into account the influence of phase contact time (1–180 min), solution pH (1–8) and temperature (20--60°C), adsorption capacities q_t (mg/g) at time t, were calculated from Eq. (1) by analogy. In order to investigate the effect of agitation speed on dye adsorption, preliminary experiments were carried out by varying the

agitation speed from 140 to 200 rpm. The highest values of q_t were obtained for the agitation speed 180 rpm. Therefore 180 rpm were used in all batch experiments.

Langmuir isotherm

The Langmuir isotherm is derived on the assumption of monolayer coverage of adsorbate over a homogenous adsorbent surface [10]. The linear form of the Langmuir isotherm Equation (2) is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{2}$$

where: C_e — equilibrium concentration of dye (mg/L),
    q_e — amount of dye sorbed per the unit mass of sorbent at equilibrium (mg/g),
    Q_0 (mg/g) and b (L/mg) — Langmuir constants related to the sorption capacity and the energy of sorption, respectively.

Freundlich isotherm

The Freundlich linearized isotherm is expressed by the following Eq. (3) [11]:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where: C_e — equilibrium concentration of dye (mg/L),
    q_e — amount of dye sorbed per the unit mass of sorbent (mg/g),
    K_F (mg/g) and n — Freundlich constants.

The values of K_F and n can be estimated from the intercept and slope of the linear plot $\log q_e$ versus $\log C_e$. K_F is the sorption capacity of the anion exchanger which can be defined as the sorption or distribution coefficient and represents the quantity of dye sorbed onto the anion exchanger for a unit equilibrium concentration. The slope $1/n$ ranging from 0 to 1 is a measure of sorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The value $1/n$ below 1 indicates a normal isotherm while above 1 is indicative of cooperative sorption [10].

Temkin-Pyzhev isotherm

Heat of sorption and the sorbent-sorbate interactions were studied by Temkin and Pyzhev. They suggested that due to these interactions the heat of sorption of all molecules in the layer decreased linearly with coverage [12]. The Temkin isotherm Equation (4) is given as:

$$q_e = \left(\frac{RT}{b_T}\right) \ln A + \left(\frac{RT}{b_T}\right) \ln C_e \tag{4}$$

where: b_T — Temkin constant related to the heat of sorption (J/mol),
    A — Temkin isotherm constant (L/g),

R — universal gas constant (8.31 J/mol K),

T — temperature (K).

Dubinin-Radushkevich isotherm

The Dubinin-Radushkevich model is often used to estimate the characteristic porosity and appearance of free energy of sorption [12]. The linear form of the Dubinin-Radushkevich equation is given as:

$$\ln q_e = \ln X_m - k_{DR}\varepsilon^2 \qquad (5)$$

where: k_{DR} — free energy of sorption obtained from the slope (mol²/kJ²),

X_m — Dubinin-Radushkevich isotherm constant (calculated from the intercept) and related to the degree of sorption (mg/g),

ε — Polanyi potential.

The mean free energy E (kJ/mol) of sorption can be computed from the following relation:

$$E = (-2k_{DR})^{-1/2} \qquad (6)$$

Kinetic studies

Three common kinetic expressions, namely, the Lagergren pseudo-first order equation (Eq. (7)), the pseudo-second order equation (Eq. (8)) as well as the Weber and Morris intraparticle diffusion model (Eq. (9)) [11, 12] were fitted to the experimental data of Sunset Yellow sorption on Amberlite FPA51:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303}t \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \qquad (8)$$

$$q_t = k_i t^{0.5} + C_i \qquad (9)$$

where: q_1 — amount of dye sorbed at equilibrium according to the pseudo-first order equation (mg/g),

q_2 — amount of dye sorbed at equilibrium according to the pseudo-second order equation (mg/g),

q_t — amount of dye sorbed at time t (mg/g),

t — time (min),

k_1 — constant rate of the pseudo-first order adsorption (1/min),

k_2 — constant rate of the pseudo-second order adsorption (g/mg min),

k_i — intraparticle diffusion rate (mg/g min^0.5),

C_i — intercept.

Results and discussion

The dye concentration and contact time between the sorbent and the dye play a significant role in the purification of wastewaters using anion exchange resins. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of the sorbent for its use in wastewater treatment. The influence of phase contact time on Sunset Yellow adsorption on Amberlite FPA51 was studied ranging the initial dye concentrations from 100 to 500 mg/L at 20°C. Figure 1 shows the effect of phase contact time on Sunset Yellow uptake from aqueous solutions of different initial concentrations by the weak base anion exchanger.
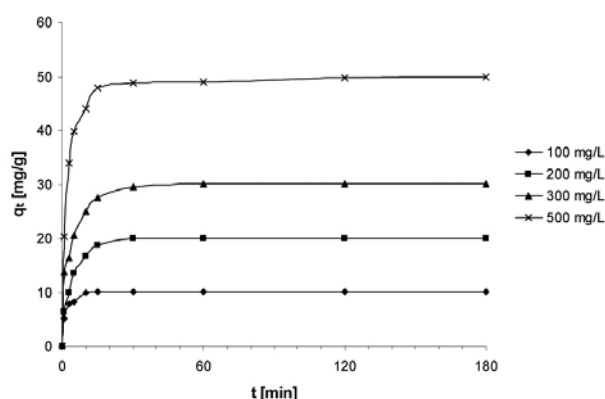

Fig. 1. Effects of phase contact time and initial concentration on removal of Sunset Yellow from aqueous solutions by Amberlite FPA51 at 20°C.

The equilibrium was reached after 20 min of phase contact time. The amounts of Sunset Yellow sorbed at equilibrium were equal to 9.9, 18.8, 29.6 and 48.7 mg/g for the dye solutions of the initial concentrations 100, 200, 300 and 500 mg/L, respectively.

The amount of Sunset Yellow sorbed by Amberlite FPA51 during the first 20 min of phase contact time slightly increased when the temperature of dye solution increased from 20 to 60°C. This may also be a result of the decrease in the thickness of the boundary layer surrounding the resin beads with the temperature, so that the mass transfer resistance of anion-exchanger in the boundary layer decreases. The fact that the sorption of the acidic dye is in favour of temperature indicates that the mobility of the dye molecules increases with the temperature rise.

The relations between the initial pH of Sunset Yellow solutions and the sorption capacity of the weakly basic anion exchanger Amberlite FPA51 were studied in the system containing 200 mg of dye per 1 L at 20°C. Decrease in the sorption capacity with the increasing of initial solution pH was observed. The q_t values slightly decreased (from 18.7 to 16.2 mg/g) with the increasing

initial solution pH from 1 to 8 because the capacity of the weak base anion exchange resin is a function of pH (it decreased with the increase of pH). Because of negligible influence of initial solution pH on Sunset Yellow uptake by Amberlite FPA51 ion-exchange mechanism in not predominant, some other mechanisms e.g. repulsion between dye-dye molecules and/or anion exchange matrix/dye molecules also play an important role. Sunset Yellow is classified as azo dye and contains groups (–OH, –N=N–) that can participate in covalent, coulombic, hydrogen bonding or in weak van der Waals interactions.

Figure 2 shows the equilibrium adsorption isotherm of Sunset Yellow and fitting of the models to the experimental data. It exhibits a steep increase at low concentrations, indicating high affinity for the solute. The adsorbed amount of the dye increased slightly, showing almost horizontal plateaus at high concentrations. The isotherm constants are summarized in Table 1. The analysis of r^2 values showed that the Langmuir and Dubinin-Radushkevich equations have more precise coefficients than the Freundlich and Temkin ones for modelling of Sunset Yellow adsorption on the weakly basic anion exchanger. The Langmuir isotherm yielded the best fit with r^2 value as compared to the other three models, r^2 for the plot of C_e/q_e vs. C_e was equal to 0.999. The maximum monolayer capacity Q_0 was 130.6 mg/g. The value of R_L was found to be in the range of 0 and 1 and confirmed the fact that the acidic dye sorption was favourable. Applicability of the Langmuir isotherm model indicates the homogeneous nature of the anion exchanger surface and formation of monolayer coverage of dye molecule on the outer surface of the anion exchanger.

Kinetic sorption of Sunset Yellow on Amberlite FPA51 was relatively well-described using the Lagergren equation. The pseudo-second expression provided the best correlation of the experimental and calculated capacities. It was confirmed by $r^2 = 0.999$. It is generally assumed that a sorption process that fits the pseudo

Table 2. Comparison of the coefficient isotherm parameters for Sunset Yellow adsorption on Amberlite FPA51.

Isotherm model	Parameters
Langmuir	
Q_0 [mg/g]	130.6
b [L/mg]	0.184
R_L	0.00361
r^2	0.999
Freundlich	
K_F [mg/g]	72
n	0.941
r^2	0.928
Temkin-Pyzhev	
A [L/g]	374.4
b_T [J/mol]	306
r^2	0.947
Dubinin-Radushkievich	
k_{DR}	0.00233
E [kJ/mol]	14.6
X_m [mg/g]	119.1
r^2	0.979

second-order kinetic equation is the one controlled by chemisorption [10–12]. The most commonly used technique for identifying the mechanism involved in the sorption is by fitting the experimental data in the intraparticle diffusion model (Eq. (9)) proposed by Weber and Morris. Multi-linearity in q_t vs. $t^{0.5}$ plot reported in literature is considered in many cases, e.g. [13]. As shown in Fig. 3, the sorption data of Sunset Yellow on Amberlite FPA51 can be fitted by two straight lines. The initial curved portion of the plot was due to external diffusion (boundary layer diffusion) while the second linear portion is the intraparticle diffusion (diffusion into the polymer network). However, the results do not pass through the origin, indicating that
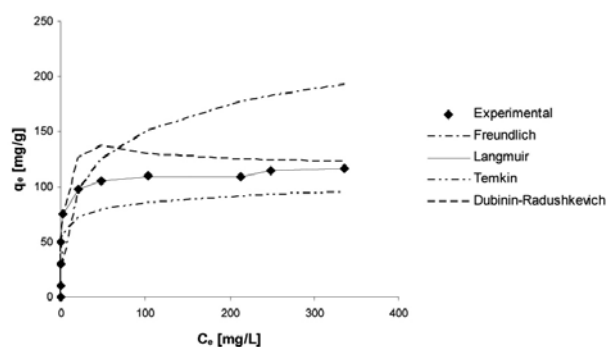

Fig. 2. Fitting of the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms to the experimental data of Sunset Yellow sorption on Amberlite FPA51 at 20°C.
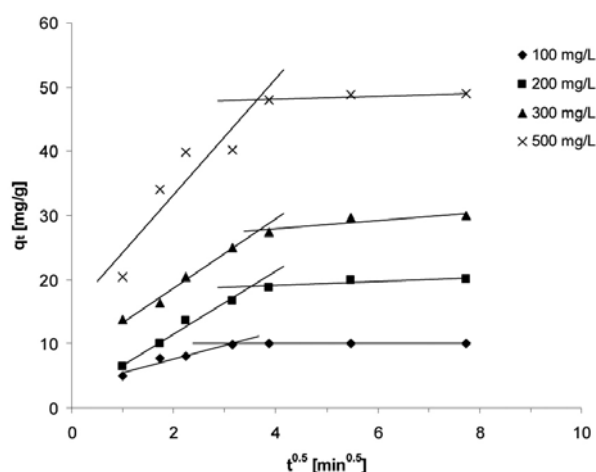

Fig. 3. Intraparticle diffusion kinetics of Sunset Yellow sorption on Amberlite FPA51 at different initial dye concentrations.

intraparticle diffusion is not the only rate-limiting mechanism and that some other mechanisms (e.g. repulsion between dye-dye molecules and/or anion exchange/dye molecules due to concentration density) also play an important role. The intercept C_i provides information about the boundary layer thickness, the larger the intercept, the greater is the boundary layer effect. The values of C_i increase from 9.9 to 47.2 mg/g with the increasing concentration. The values of intraparticle diffusion rate constants k_{id} calculated from the second portion of the plot q_t vs. $t^{0.5}$ changed from 0.008 to 0.626 mg/g min$^{0.5}$. The values of r^2 were in the range 0.636–0.829.

Conclusions

In this study, the potential of the weakly basic anion exchange resin (Amberlite FPA51) for the treatment of Sunset Yellow solutions was evaluated. The weak base anion exchanger of macroporous structure — Amberlite FPA51 can find practical application in purification of wastewaters containing Sunset Yellow.

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