

# Sorption of the acid dyes onto strongly basic anion exchanger: Kinetic and equilibrium studies

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The strong base acrylic anion exchangers, Amberlite IRA-458, was used as an adsorbent for the investigation of acid dyes (Acid Orange 7, Acid Orange 10 and Acid Red 88) adsorption kinetics and isotherms. The pseudo-first order and pseudo-second order kinetic models were used to analyze the kinetic data and good agreement between the experimental and calculated amounts of dye adsorbed at equilibrium were obtained for the pseudo-second order kinetic models for the entire investigated concentrations domain in the case all three investigated dyes. The adsorption equilibrium data were analyzed by the Langmuir and Freundlich isotherm models with the best fitting being the first one.

**Keywords and phrases:** adsorption isotherms, adsorption kinetics, acid dyes, resin.

## Introduction

Wastewaters from food colouring, cosmetics, paper and textile industries are polluted by dyes. When these coloured effluents enter rivers or any other surface water system they upset biological activity. Ground-water systems are also affected by these pollutants because of leaching from soil. Dyes can cause allergic dermatitis, skin irritation, cancer and mutation [1]. As regulation become more stringent, complicated and multi-step treatment for the raw dye wastewater is required and the removal of dyes is usually the key point. [2]. Therefore, the treatment of such wastewater containing soluble dyes requires complete removal followed by secure disposal [3]. There are several methods for dye removal such as biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation and photocatalytic processes, membrane processes and adsorption [2]. The sorption process under certain conditions has a definite edge over other methods used for dyes recovery, because of its simplicity, selectivity and efficiency [4]. Currently, the most used adsorption agent in industry is activated carbon, which was successfully tested also for the removal of dye from water. However, relatively high operating costs and problems with regeneration of the spent activated carbon hamper its large-scale application [5].

The good sorption results with the anion exchangers suggest that these materials in general could be efficient sorbents for dye removal. They are not lost during the regeneration, recovery of solvent after use, and the removal of soluble dyes what is the main advantage of using them but they suffer from drawbacks such as their high price of manufacturing [5].

As the extension of anion exchangers as an adsorbent to remove acid dyes from water has seldom been explored, its dye removal properties should be investigated. Acid dyes are sodium salts of organic sulphonic acids. Brightly coloured, water soluble and reactive acid dyes are composed of ionizable anionic groups such as sulphonates, carboxylates or sulphates. Acid dyes have a direct affinity towards polyamide and protein fibers in an acidic dye bath so these dyes are commonly used for dyeing polyamide fibers such as well as silk, wool and modified acrylics. Acid dye bath wastewaters are characterized by high chemical oxygen demand (COD), dissolved solids, high temperature and acidic pH. Moreover, acid dyes are the most problematic with their high molecular weight, as they tend to pass through conventional treatment systems unaffected [6].

The aim of this study was to determine the efficiency of the removal of acid dyes, namely Acid Orange 7, Acid Orange 10 and Acid Red 88 from water solution with

an weak base anion exchange resin with an gel structure based on the acrylic-crosslinked copolymers, namely Amberlite IRA-458 resin.

## Materials and methods

### Materials

Deionized water was used for preparation of all solutions and for dilution of wastewater samples. Acid dyes were supplied by Sigma-Aldrich, Germany. Figure 1 shows the structure of dyes. In Table 1 their characteristics are summarized. The dye was used as supplied without purification, and the fraction of inert material was not taken into account in the calculation of dye concentration.

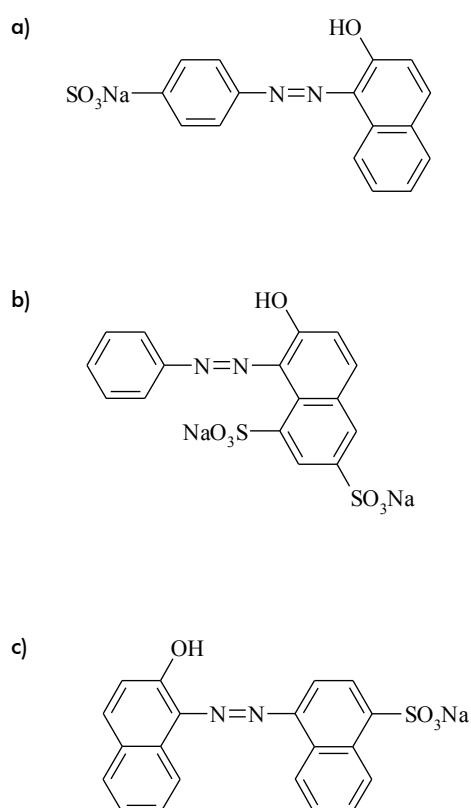


Fig. 1. Chemical structure of a) Acid Orange 7, b) Acid Orange 10, c) Acid Red 88.

Table 1. Properties of acid dyes.

Name	Molecular weight (g/mol)	$\lambda_{\max}$ (nm)	Molecular formula
Acid Orange 7	350.33	484	$C_{16}H_{11}N_2NaO_4S$
Acid Orange 10	452.38	478	$C_{16}H_{10}N_2Na_2O_7S_2$
Acid Red 88	400.38	502	$C_{20}H_{13}N_2NaO_4S$

The anion exchanger-strong basic resins Amberlite IRA-458 was supplied by Rohm and Haas, France. It is an

acrylic gel type strongly basic anion exchange resin, with unique chemical and physical properties. It combines high operating capacity and low silica leakage values. The acrylic structure of Amberlite IRA-458 resin allows for the effective adsorption during the service run and good desorption during regeneration of the naturally occurring organic molecules present in many water supplies. Its characteristic is compiled in Table 2.

Table 2. Anion exchanger characteristics.

Description	Amberlite IRA-458
Type	Strong base
Functional group	Quaternary ammonium
Matrix	Crosslinked acrylic gel structure
Physical form	Translucent white spherical beads
Ionic form as shipped	Chloride
Total exchange capacity	$\geq 1.25$ eq/dm <sup>3</sup> (Cl <sup>-</sup> form)
Moisture holding capacity	57 to 64% (Cl <sup>-</sup> form)
Harmonic mean size	600 to 900 $\mu$ m
Maximum operating temperature	35°C
Operating pH	0 to 14

### Sorption kinetics

For the kinetic studies, 20 mL acid dye solution at a respective initial dye concentration varying from 100–300 mg/L was introduced into a 100 mL joint-stopper conical flask containing 0.2 g of the dried anion exchanger. The flask was capped and agitated at a constant temperature of 25°C in the thermostatic shaker (Elphin +358S, Poland) at 180 rpm for 1–240 min. After that time, the resin was filtered off and the concentration of the residual dye was determined spectrophotometrically at the maximum absorbance wavelength using an UV-VIS spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany). The amount of solute adsorbed at time  $t$ ,  $q_t$  was calculated as:

$$q_t = \frac{(c_0 - c_t)}{w} \times V \quad (1)$$

where:  $c_0$  — (mg/dm<sup>3</sup>) is the liquid-phase concentrations of solutes at the initial time;

$c_t$  — (mg/dm<sup>3</sup>) are the liquid-phase concentrations of solutes at the given time  $t$ ;

$v$  — (dm<sup>3</sup>) is the volume of solution;

$w$  — (g) is the mass of dry resin.

### Sorption isotherms

For adsorption isotherms, 0.2 g of the dried anion exchanger was equilibrated separately with 20 mL solutions containing different acid dye concentrations (50–24000 mg/L) in a 100 mL joint-stopper conical

flask. The contents were shaken thoroughly at temperatures of 25°C using a thermostatic shaker (Elphin +358S, Poland) rotating at 180 rpm. The solutions were then filtered and the equilibrium concentrations of acid dye concentrations were determined using the UV/VIS spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany). The amount of solute adsorbed at equilibrium,  $q_e$  was calculated as:

$$q_e = \frac{(c_0 - c_e)}{w} \times V \quad (2)$$

where:  $c_0$  — (mg/dm<sup>3</sup>) is the liquid-phase concentration of solutes at the initial time;

$c_e$  — (mg/dm<sup>3</sup>) is the liquid-phase concentration of solutes at equilibrium;

$v$  — (dm<sup>3</sup>) is the volume of solution;

$w$  — (g) is the mass of dry resin.

## Results and discussion

From Fig. 2, it is obvious that the amount of the adsorbed dye on Amberlite IRA-458 increases with time.

In the case Acid Orange 7 and Acid Orange 10 adsorption on Amberlite IRA-458, the process is very fast and the dye is quantitatively removed in 20 min in the whole examined range of the initial dye concentration. In the case Acid Red 88, the sorption rate was rapid for the first 20 min and the equilibrium state of sorption was achieved for the dye solutions of the initial concentration of 100 mg/dm<sup>3</sup>. The time of contact phase necessary to reach equilibrium in the case of higher concentrations of Acid Red 88 was longer and equaled 180 min. for the initial dye concentrations of 400 mg/dm<sup>3</sup>.

In order to investigate the mechanism sorption and potential rate controlling step, reaction-based kinetic models were used to test experimental data concerning investigated acid dyes sorption on Amberlite IRA-458. The pseudo-first order Lagergren model, traditionally used for describing sorption kinetics, is described by equation (3):

$$\log(q_e - q_{t1}) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

where:  $q_e$  — (mg/g) is the amount of dye adsorbed at equilibrium;

$q_{t1}$  — (mg/g) is the amount of dye adsorbed at time  $t$ ;

$k_1$  — (1/min) is the rate constant of pseudo first-order sorption.

A straight line of  $\log(q_e - q_{t1})$  vs.  $t$  suggests the applicability of this kinetic model and the values of  $\log q_1$  and  $k_1$  can be determined by the intercept and the slope of this linear plot respectively [7, 8].

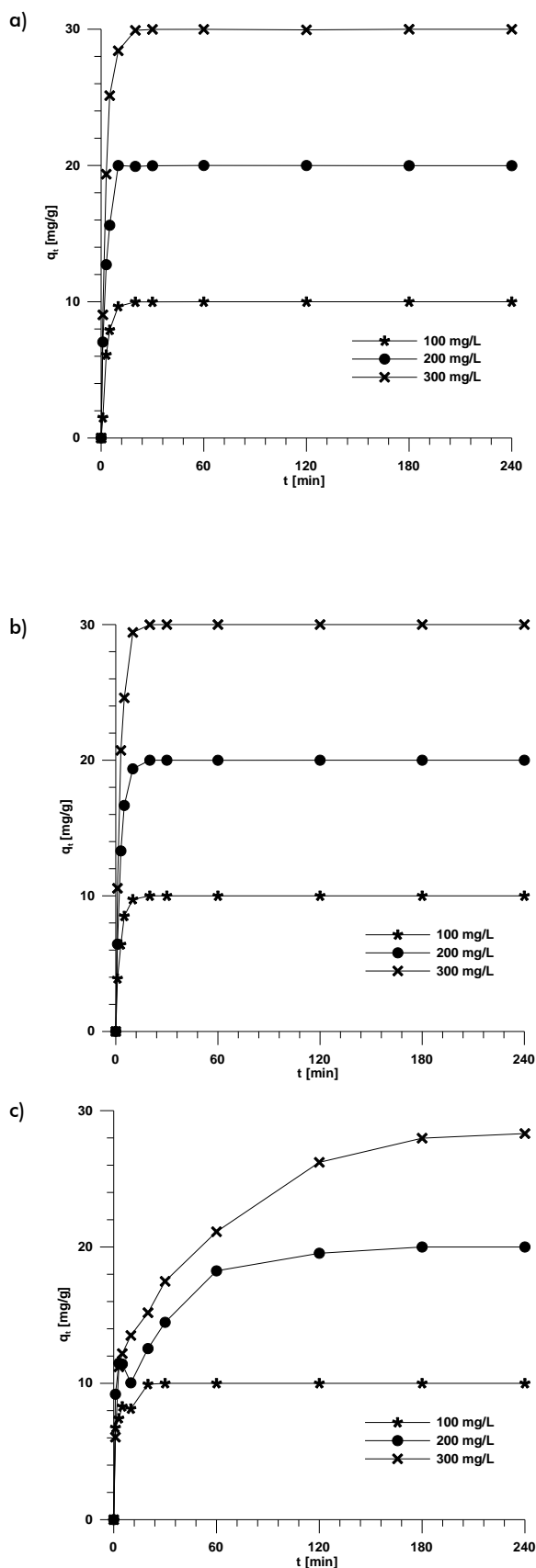


Fig. 2. The effect of phase contact time on sorption of a) Acid Orange 7, b) Acid Orange 10 and c) Acid Red 88 on Amberlite IRA-458.

According to the pseudo-second order model the dye sorption kinetic is described by the following equation:

$$\frac{t}{q_{t2}} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where:  $q_{t2}$  — (mg/g) is the amount of dye adsorbed at time  $t$ ;

$k_2$  — (g/mg min) is the equilibrium rate constant of pseudo second-order sorption.

If pseudo second-order kinetics is applicable, the plot of  $t/q$  against  $t$  of equation (3) should give a linear relationship, from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of the plot and there is no need to know any parameters beforehand [7, 8].

The results of table 3 show that the correlation coefficients ( $r^2$ ) for the pseudo-second order kinetic equation were closer to 1.0 for all cases, and the calculated  $q_{exp}$  values are closer to the experimental data than the calculated values of pseudo-first order model. This observations demonstrated that the sorption of the acid dyes on Amberlite IRA-458 follows a pseudo-second order rate equation and suggested that chemical sorption instead of mass transfer is the rate limiting step for the sorption process.

Proper analysis and design of adsorption processes requires relevant adsorption equilibria as one of the vital information. In equilibrium, a certain relationship prevails between solute concentration in solution adsorbed state (i.e. the amount of solute adsorbed per unit mass of adsorbent). Their equilibrium concentrations are a function of temperature. Therefore, the adsorption equilibrium relationship at given temperature is referred as adsorption isotherm. Several isotherm equations are available and two of them are selected in this study, Langmuir and Freundlich isotherms [9].

The Langmuir isotherm is based on the assumption that adsorption takes place at specific homogenous sites

within the adsorbent and there is no significant interaction among adsorbed species and that the adsorbent is saturated after one layer of adsorbent molecules formed on the adsorbent surface. The linearized Langmuir isotherm equation can be written as follows:

$$\frac{c_e}{q_e} = \frac{1}{q_0 b} + \frac{c_e}{q_0} \quad (5)$$

where:  $q_0$  — (mg/g) is the maximum capacity of adsorbate to form a complete monolayer on the surface;

$b$  — the Langmuir constant related to the energy of adsorption (L/mg).

By plotting  $c_e/q_e$  versus  $c_e$ , it is possible to obtain the value of  $q_0$  from the slope which is  $1/q_0$  and  $b$  from the intercept which is  $1/q_0 b$  [10].

The Freundlich isotherm model takes the multilayer and heterogenous adsorption into account. Its linearized form can be given as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e \quad (6)$$

where:  $K_F$  — (mg/g) is the Freundlich constant related to the adsorption capacity of the adsorbent;

$1/n$  — another constant related to the surface heterogeneity.

The plot of  $\log q_e$  versus  $\log c_e$  should give a straight line with a slope of  $1/n$  and the intercept of  $\log K_F$ .

The parameters of these adsorption isotherms evaluated from the linear plots are presented in Table 4. The adsorption isotherm was favourable and obeyed the Langmuir expression what is confirmed by high values the correlation coefficient.

Conformation of the experimental data into Langmuir isotherm equation indicated the homogenous

Table 3. Kinetic parameters for the effect of solution concentrations.

Concentration (mg/dm <sup>3</sup> )	$q_{e,exp}$ (mg/g)	Pseudo-first order kinetic			Pseudo-second order kinetic		
		$q_{e,cal}$ (mg/g)	$k_1$ (1/min.)	$r^2$	$q_{e,cal}$ (mg/g)	$k_2$ (g/mg min)	$r^2$
Acid Orange 7							
100	10.00	2.39	0.140	0.795	10.14	0.058	0.999
200	19.99	16.77	0.271	0.999	20.13	0.055	0.999
300	29.99	1.73	0.052	0.402	30.22	0.033	0.999
Acid Orange 10							
100	10.00	9.33	0.357	0.996	10.06	0.226	0.999
200	20.00	18.63	0.339	0.999	20.14	0.056	0.999
300	30.00	33.98	0.412	0.998	30.19	0.041	0.999
Acid Red 88							
100	10.00	5.27	0.199	0.885	10.06	0.115	0.999
200	20.00	10.97	0.027	0.981	20.62	0.007	0.995
300	28.32	19.68	0.007	0.894	27.02	0.002	0.914

Table 4. Langmuir and Freundlich isotherm parameters.

Dyes	Langmuir isotherms			Freundlich isotherms		
	q <sub>0</sub> [mg/g]	b [dm <sup>3</sup> /g]	r <sup>2</sup>	n	K <sub>F</sub> [mg/g]	r <sup>2</sup>
Acid Orange 7	499.27	0.262	0.997	12.77	261.95	0.672
Acid Orange 10	975.54	0.065	0.999	6.76	313.54	0.796
Acid Red 88	53.08	0.008	0.978	5.29	11.74	0.778

nature of Amberlite IRA-458, i.e. each dye molecule/anion exchanger adsorption has equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of dye molecule at the outer surface of Amberlite IRA-458.

Amberlite IRA-458 has large adsorption capacity of 975.54 mg/g for Acid Orange 10 if compared to data obtained for other investigated acid dyes.

## Conclusion

The effect of hydrophobic properties of the dyes on the affinity to Amberlite IRA-458 is apparent: the greater the hydrophobicity (lesser number of sulpho, greater number of aromatic rings in molecule), the less affinity to the anion exchanger. The series of affinity of the examined acid dyes to the quaternary ammonium groups of Amberlite IRA-458 is as following:

Acid Orange 10 > Acid Orange 7 > Acid Red 88

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