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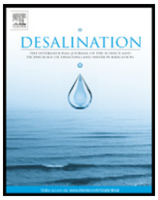

# Efficient removal of Acid Orange 7 dye from water using the strongly basic anion exchange resin Amberlite IRA-958

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ABSTRACT

The removal of Acid Orange 7 dye from water using the macroporous strongly basic anion exchange resin was investigated using the batch method with a particular reference to the effects of the initial dye concentration, the phase contact time, temperature, pH, the presence of inorganic salts ($NaH_2PO_4$, $Na_2HPO_4$, $Na_2SO_4$) and surfactants (SDS, CTAB, Triton-100) on adsorption. Next, the desorption of the dye adsorbed on the anion exchanger was studied using the batch method by testing different solutions, namely aqueous and aqueous–methanol solutions of HCl, NaOH, and NaCl. Also the anion exchanger behavior with artificial and real wastewater samples was studied with very promising results.

## 1. Introduction

Natural colorants have been used since prehistoric times, as reflected by the cave drawings in Europe (Altamira, Spain, Grotto Chauvet, France), Africa (Zimbabwe), ancient Egypt, and China (terracotta Army, Xian). The sites in Egypt and China are especially remarkable because the oldest known synthetic pigments were found there, namely Egyptian Blue, Han Blue and Han Purple. In 1856, Perkin's discovery of mauve marked the start of the modern synthetic dye industry. In the last 145 years, several million different colored compounds have been synthesized, with ca. 15,000 colorants over time, produced on a commercial scale. The annual worldwide production of dyes is approximated at 800,000 tonnes and about 50% of these are azo dyes [1,2].

Anionic azo dyes contain many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g. azoic, antraquinone, triphenylmethane, and nitro dyes) possessing water-solubilizing, ionic substituents as a common feature. The presence of strongly water-solubilizing substituents, especially sulfonate ($SO_3^-$) groups, is characteristic of this class. Aromatic sulfonates are not only easily accessible synthetically but they also possess the advantage of being negatively charged in aqueous solution over an extremely broad pH range. Anionic monoazo dyes and their metal salts are widely used for either dyeing paper and leather, or as pigments. Their main application, however, constitutes the dyeing of protein (wool, silk) and synthetic polyamide fibers. In this context, the term acid dye is often used, since the corresponding dyeing process takes place in weakly acidic solution (pH 2–6). The acid dyes have no affinity for vegetable fibers, no fixed bond is formed and virtually no charge-transfer complex is found [1,3,4].

Among the acid monoazo dyes there are a number of much used wool dyes that possess no outstanding coloristic properties but are distinguished by brilliance of shade, very good leveling power, and particularly low cost, while their wash- and lightfastness meet only low to medium requirements. Partly influenced by the introduction of the International Wool Label to label high-quality wool articles, the fastness requirements have risen considerably, and this has necessitated the development and manufacture of particularly fast dyes. For this reason many, and above all the older, acid dyes have lost all importance for the dyeing of wool and are used today only for the coloring of paper, soaps, food and cosmetics. A long known, inexpensive, but only moderately fast dye is C.I Acid Orange 7 (Orange II). As a wool dye it is now of secondary importance, however, it is used in special areas such as leather dyeing and paper coloration. Like most other azo dyes, it tends to be disposed in industrial wastewater and poses a severe health threat to humans. It is highly toxic, and its ingestion can cause eye, skin, mucous membrane, and upper respiratory tract irritation; severe headaches; nausea; water-borne diseases such as dermatitis; and loss of bone marrow leading to anemia. Its consumption can also prove fatal, as it is carcinogenic in nature and can lead to tumors. It has now been well established that the main cause of its chronic toxicity is the electron-withdrawing character of the azo group, which develops an electron deficiency and becomes reduced to carcinogenic amino compounds. The reduction of Acid Orange 7 produces 1-amino-2-naphthol, which has been reported to induce bladder tumors. Orange II can also easily undergo enzymatic breakdown along with reduction and cleavage to give aromatic amines, which, upon exposure, can cause methemoglobinemia. The intermediate amines thus formed also tend to oxidize the

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heme iron of hemoglobin from Fe(II) to Fe(III) and block oxygen binding, resulting in some characteristic symptoms such as cyanosis of lip and nose, weakness, and dizziness. When Acid Orange 7 enters the human body through ingestion, it is considered genotoxic; however, if some impurities, such as aromatic amines, are present, it shows mutagenic activity. Due to large amounts of Acid Orange 7 consumption, it is essential to have a proper method to remove this dye from wastewater in order to avoid potential threat for the environment. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, also Acid Orange 7 does not decompose biologically, and resists to light irradiation and chemical oxidation. However, the adsorption of this dye on efficient solid supports is considered as a simple and economical method for its removal from water and wastewater providing sludge-free cleaning operations and many studies have been conducted to find suitable adsorbents to reduce Acid Orange 7 concentration [3–12]. They have included spent brewery grains [13], guava seed carbon [14], de-oiled soya [5], bottom ash [5], sludge [15], activated carbon fibers [15] ethylenediamine-modified magnetic chitosan nanoparticles [16], diethylenetriamine-modified native as well as enzymatic and hydrolyses starch [17], copper(II) complex of dithiocarbamate-modified starch [18], titania aerogels [19], titanium dioxide [20], unmodified and surfactant modified zeolites [21], soil [22], and Sahara desert sand [23].

Because a number of exchange resins have been used quite efficiently for the removal of specific organic compounds [24], this study investigates the adsorption characteristics of Acid Orange 7 dye on the strongly basic polyacrylic anion exchanger Amberlite IRA-958 of macroporous structure. First, the present paper describes the dye adsorption behavior on the anion exchanger in terms of the initial dye concentration, the phase contact time, initial pH of the solution, temperature, ionic strength and surfactant type. Next, the batch desorption results for different desorption solutions used for the anion exchanger regeneration are demonstrated. Finally, the studies on color removal from model and real textile wastewater containing acid dyes are presented.

## 2. Experimental

### 2.1. Materials

The 4-(2-hydroxy-1-napthylazo) benzene sulfonic acid sodium salt, commonly named acid Orange 7, synonymous with Orange II was used in the study. In aqueous solutions, Acid Orange 7 being a hydroxyazo dye, exists as mixture of azo and hydrazone tautomers being in the equilibrium due to very rapid intramolecular proton transfer [25]. The general characteristics of the dye are presented in Table 1. The dye was obtained from Sigma-Aldrich (Germany) with 90% purity and used as supplied without further purification. The fraction of inert material was not taken into account in the calculation of dye concentrations. All other chemicals used were also of analytical grade. $NaH_2PO_4$, $Na_2HPO_4$, $Na_2SO_4$, NaCl, HCl and NaOH were purchased from POCh (Poland) and SDS, CTAB and Triton X-100 surfactants were supplied by Sigma-Aldrich (Germany). The dye solutions without any addition were prepared by dissolving a defined quantity of the dye in distilled water. The dye solution with the given salt or surfactant was prepared by dissolving the appropriate amount of salt or surfactant in distilled water and adding the proper amount of dye to produce a dye solution of 200 mg/L concentration.

The artificial wastewater was prepared by mixing four dyes in equal amounts each of them of 0.1 g/L with the dyeing auxiliaries. The composition of this wastewater is reported in Table 2.

Real textile effluents were supplied by a dye-house located in Milan, Italy. The wastewater sample with code ANTI had reddish color and the following characteristics: pH 3.48, conductivity 13.49 MV, $BZT_5$ 229 mg/$dm^3$, ChZT 13,440 mg/$dm^3$.

The commercially available and economically reasonable strong base anion exchange resin, Amberlite IRA-958 was obtained from Rohm and Haas (France) in the chloride form. This is a macroreticular strongly basic anion exchanger having quaternary ammonium functionality in a crosslinked acrylic polymer matrix, with an ion exchange capacity of 4.1 meq/g of dry resin (0.8 meq/mL of wet resin), the particle size between 0.67 and 0.85 mm, the average pore diameter of 6.46 nm and the BET surface area of 2.03 $m^2$/g [26]. The resin was washed with both HCl (0.1 M) and distilled water to remove impurities from its synthesis and finally air-dried.

### 2.2. Batch adsorption/desorption studies

Batch experiments were used in the present study in order to achieve the optimum operating conditions for the treatment process. The appropriate aqueous phase (20 mL) and the anion exchanger (0.2 g) were put into a conical flask and shaken mechanically using the laboratory shaker Elpin type 357 (Poland) with an intensity of agitation of 180 rps. After the predetermined time, the anion exchanger was removed by the filtration. In order to determine adsorption as a function of time, the samples of the anion exchanger were contacting with the dye solution at six different initial dye concentrations (50, 100, 200, 300, 400, 500 mg/L) for 1–240 min ($pH = 5.80$, $T = 298$ K). In the pH experiments, the pH of the dye solution at the initial concentration of 200 mg/L was adjusted with HCl and NaOH at various pH values of 2–12 and the obtained dye solutions together with the anion exchanger were agitated for an equilibrium time of 180 min at 298 K. In separate series of the experiment, the amount of salts or surfactants necessary to obtain the concentration of 0.1, 0.5, 1 and 2 g/L was added to the dye solution at the concentration of 200 mg/L and the studies were conducted by the same procedures as in the case of pH studies. Adsorption experiments were also carried out to obtain isotherms at different temperatures (298, 308 and 318 K) by shaking the anion exchanger with the dye solution at the concentrations from 9000 to 23,000 mg/L for an equilibrium time of 24 h ($pH = 5.80$).

Next, in order to obtain the desorption data and determine the suitable desorption solution, the desorption experiments were carried out. First, the anion exchanger was contacted with the dye solution at high concentration of 23,000 mg/L for 24 h at room temperature. Then the anion exchanger loaded with the dye was filtered, washed gently in distilled water to remove the unadsorbed dye and air dried. The samples of the obtained anion exchange resin were agitated with different desorption solutions (NaCl, NaOH, HCl solutions, methanol solutions and NaCl–methanol, NaOH–methanol and HCl–methanol mixtures) for 8 h at room temperature.

### 2.3. Color removal of model and real textile wastewater studies

The color removal of model and real textile wastewaters containing acid dyes was studied using the batch method. In this experiment the dosage of 0.5 g of the anion exchanger was shaken with 50 mL of acid dye model wastewater solution or acid dye real wastewater solution for 1 min to 96 h. The real textile wastewater solution was 50 times diluted. During this experiment, small samples were withdrawn from the conical flasks at various times in order to estimate the removal of dyestuff.

### 2.4. Analyses

The dye concentration in the clear supernatant after proper dilution was determined using the UV–Vis spectrophotometer (Specord M 42, Carl Zeiss Jena, Germany).

In the case of the dye adsorption/desorption studies, the dye concentration was measured at the maximum absorption wavelength in the visible range and estimated quantitatively using a linear regression equation obtained by plotting a proper calibration curve over a range of concentrations. Various calibration curves for different