

Removal of Direct Red 81 from Aqueous Solution Using an Acidic Soil Containing Iron (Case Study of Lahijan Soil)

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ABSTRACT: Direct Red 81, a dye widely used in textile industries, is frequently detected dye in water resources. High costs, the formation of hazardous byproducts, and high energy costs restrict the use of some removal methods. Therefore, the main objectives of this research are the feasibility of using soil containing iron as a low cost adsorbent to remove (Direct Red 81) from the aqueous phase and determining the optimum conditions for maximum removal efficiency. The present study was conducted at a bench scale. The influence of different parameters including the number of adsorbents; initial concentration of dye solution and pH at different time intervals on dye removal efficiency were investigated. The maximum removal rate of dye (84%) occurred in pH=7 in the presence of 1 g soil with the initial dye concentration of 50 mg/L at 30 min reaction time. Moreover, due to the effect of acidic pH and the iron content of used soil a significant increase was observed in the rate of Direct Red 81 dye removal. In conclusion, using soil containing iron is an appropriate method for the removal of Direct Red 81 from aqueous solutions.

KEYWORDS: Adsorption; Dye removal; Direct Red 81; Aqueous solution; Soil containing iron.

INTRODUCTION

Environmental pollution caused by industrial wastes is very important due to toxicity and danger to human health and the environment [1-3]. Dyes are one of the most important pollutants in water sources [4], which mostly exist in the wastewater from textile, leather,

food processing, dyeing, paper, and paint industries [5, 6]. Azo dyes are aromatic compounds with one or more groups of -N = N- [7, 8] that are widely used, especially in the textile industries [9, 10].

These dyes are the most important pollutants in textile

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waste and it is estimated that about 15% of them enter wastewater during manufacturing and processing operations [11-13].

Many different methods such as photochemical oxidation, Nano filtration and Ultrafiltration, Ozonation, reverse osmosis, chemical coagulation, electrochemical degradation [14-16], integrated chemical/biological degradation, and solar photo-Fenton [17-19] are used for the removal of dye from industrial wastewater. High costs, the formation of hazardous byproducts and requires great amount of energy are the limiting factors of these removal methods [20]. Adsorption process at controlled conditions is one of the most effective methods for the removal of recalcitrant organic pollutants from the aquatic environment [21-23].

One of the most common adsorbents is activated carbon, but high price and limited availability restrict its usage. Therefore, many types of research have been conducted to find an alternative material with low cost; wood, ash, straw, pug [24], orange skin [25] and rice husk [26] are some adsorbents.

In recent years, iron powder has been widely used as a reducing agent in promoting environmental conditions. Among different pollutants, Azo dyes are easily degraded by iron powder [5]. In this study, the removal of Direct Red 81 from aqueous solution by using soil containing iron is studied under different conditions and optimum conditions for maximum removal are investigated.

EXPERIMENTAL SECTION

Chemicals and Analytical Method

All chemicals used were of reagent grade and purchased from Merck (Germany). DR 81 dye ($C_{29}H_{19}N_5Na_2O_8S_2$) with the molecular weight 675.6 g mole⁻¹ was supplied by Hoechst Company, Germany. Stock solutions of DR81 were prepared by dissolving 1g of dye in 1 lit of double distilled water. Spectrophotometer (DR 5000) at the wavelength of 510 nm was used in this study to determine Direct Red 81 residual concentration in soil samples according to the standard method (2120) [27].

Soil physiochemical characteristics

The general physiochemical characteristics of the soil were determined. Hydrometer was used to determine soil textures using Guelph method. Other soil characteristics

such as soil solution pH [28], Organic matter Content (OC) [29], Cation Exchange Capacity (CEC) [30] and Electrical Conductivity (EC) [31] were determined.

Soil sampling procedure

Soil samples were collected with a hand-driven soil auger (soil depths 0- 30 cm) from the rice farm in Lahijan in Gilan province of Iran, is located in the north of Iran. The soil sample was transported to the laboratory in zipped plastic bags and was kept frozen at -20°C until it was ready for the analysis. The soil samples were thawed and air-dried at dark in room temperature and screened through a 2.0 mm sieve for maintaining homogeneity of soil in order to reduce the variability of adsorption data. Then, it was put in the oven for 2 hr at 104°C until constant weight. Afterwards, it was stored in a desiccator for further analysis. The soil texture in Lahijan rice field was clay loamy. Soil pH and EC were 5.91 and 1.17 ds/m respectively. Organic matter Content (OC) and CEC in soil were 95% and 19.3 C mole(+)/kg soil, respectively. The native soil characteristics at Lahijan site was Clay loamy, mixed, thermic Typic Hapludults.

Data regarding the physiochemical properties of the soil showed that the Organic matter Content (OC) of the soil was high. Therefore, the effect of organic matter on adsorption was also high. Regarding the soil texture, it should be noted that the clay content has a large effect on adsorption. The effect of clay content on adsorption was between medium to high. The soil pH was acidic and the iron content in the soil was 36.5 mg/kg soil.

Adsorption experiments

This study was conducted on a laboratory scale. All the tests were performed at room temperature and normal pressure. The number of samples was determined; with one factor at the time method.

The studied parameters were pH (3, 7, and 11), initial dye concentration (10, 30, 50, 100, and 150, (mg/L)), and amount of soil (0.5, 1, 1.5, and 2 (mg/L)) at different reaction times (30, 60, and 90 min). The optimal conditions were determined according to the maximum dye removal efficiency. At first, pH was optimized by changing it. Then considering the optimal pH, the dye concentration, soil weight, and time were optimized. pH of the solutions were adjusted to the desired values using HCl and NaOH.

100 mL of dye solution was added to the soil sample and shaken in a reciprocal shaker (250 rpm). The samples were centrifuged at 300 rpm for 10 min and then filtered through whatman filter paper. After filtration, the residual dye concentrations were collected and transferred to a 15 mL glass vial and stored in a refrigerator prior to spectrophotometric analysis. Dye recovery percent from soil with this method of extraction was 98%.

Adsorption of dye was calculated using the following equation.

$$\%R = \frac{(C_i - C_f)}{C_f} \times 100 \quad (1)$$

Where R is % of dye removal

C_i (mg/g) is the initial dye concentrations

C_f (mg/g) is the residual dye concentrations

The effects of different parameters (pH, initial dye concentration, amount of soil, and reaction time) on the reduction rate of dye were determined at three replications. All the data were presented based on mean.

RESULT AND DISCUSSION

In this study, the effects of pH, initial dye concentration, adsorbent dosage, and contact time were studied in order to optimize each parameter for maximum removals. The results of adsorption and percentage of removal at different pH levels, amount of soil, dye concentration, and shaking times are shown in Figs. 1-4.

Effect of pH

pH value of the dye solution plays an important role in the adsorption process, particularly adsorption capacity [1, 19]. In Fig. 1, it is seen that absorption efficiencies increased from pH 3 to pH 7 and then declined with further increase in pH. The maximum equilibrium uptake value was found to be 84% at pH 7.

The Direct Red adsorption by soil containing iron was significantly affected by the pH range of 6-7. The pH of the system influenced the adsorption rate due to its influence on the surface properties of the adsorbent and ionization of the adsorbate molecule [25]. Therefore, the interaction between a dye and adsorbent is mainly affected by the ionization states of the functional groups on both dye molecule and adsorbent surface [21].

At higher pH (>7), increased pH value (basic condition) led to the increasing number of negatively charged sites and decreased the number of positively

charged sites. A negatively charged surface site on the soil is not favorable for the adsorption of anionic DR molecules due to the electrostatic repulsion [5, 25].

Similar results have been observed for the adsorption of Direct Blue 71 from aqueous solution by wheat shells [5].

Effect of dye concentration

To study the influence of initial dye concentration on the degradation rate, the experiments were carried out at different dye concentrations (10, 30, 50, 100, and 150 mg/L) at pH 7 and 1 g of soil for 30 min.

As shown in Fig. 2, at contact time 30 min, when the dye concentration was changed from 10 to 50, the removal percentage increased, however, removal efficiency decreased from 50 to 150 mg/L. The maximum adsorption (84 %) was obtained at the dye concentration of 50 mg/L. The percentage removal of DR81 dye was swift at the beginning of the adsorption process and then declined. The adsorption capacity increased when the initial dye concentration increased from 10 to 50 mg/L. It is also shown in Fig. 2 that the percentage removal of DR 81 dye decreased from 84% to 15% as dye concentrations increased from 50 to 150 mg/L. This result showed that, as more sites in the soil were filled, it became increasingly difficult for the dye molecules to find a vacant site [21].

Similar results [24] and inverse results [1] have been reported in the literature.

Effect of the soil amount as adsorbent

Adsorption of DR 81 on soil was studied by changing the quantity of soil as adsorbent (0.5, 1, 1.5, and 2 g) in the test solution while keeping pH (7) and initial DR 81 concentration (50 mg/L) constant at contact times for 30 min (Fig. 3).

As displayed in Fig. 3, when the amount of soil increased from 0.5 to 1 g, the removal rate increased from 12% to 84%; afterwards, the removal efficiency decreased by increasing the amount of soil. Although an increase in removal rate was observed at 2 g of soil, however, it was not significant. So, the maximum adsorption (84 %) was seen at 1 g of soil after 30 min contact at pH =7 at the dye concentration of 50 mg/L.

At first, an increase in the adsorption with adsorbent dose can be attributed to increased soil surface area and availability of more adsorption sites [22]; but afterwards,

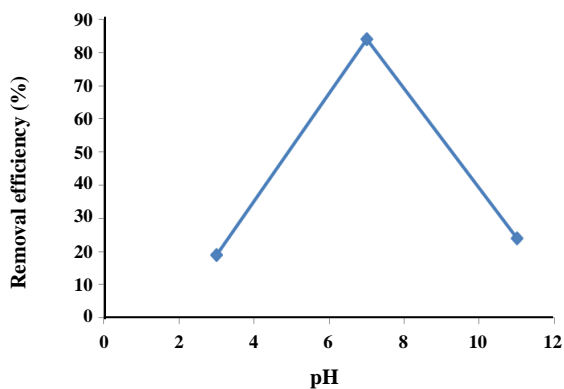


Fig. 1: Removal efficiency of dye from aqueous solution at different pH (dye concentration = 50 mg/L, amount of soil= 1 g, contact time = 30 min).

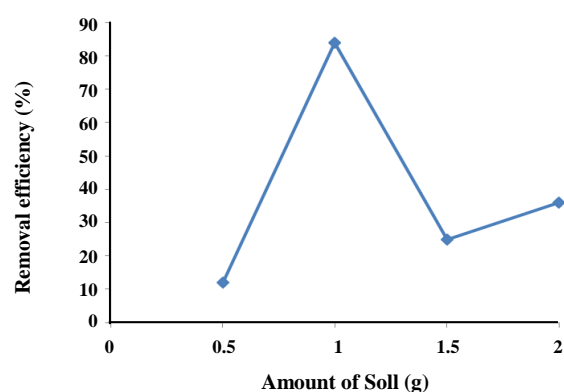


Fig. 3: Removal efficiency of dye from aqueous solution at different amounts of soil (pH =7, dye concentration= 50 mg/L, contact time = 30 min).

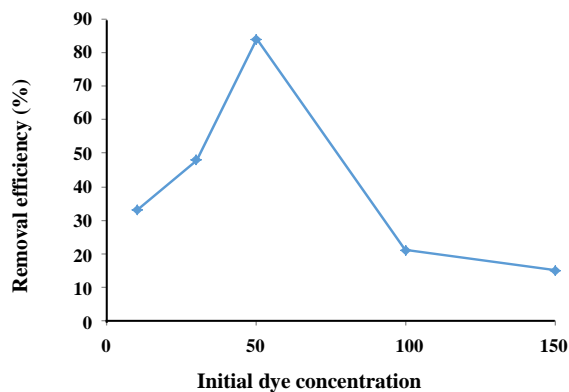


Fig. 2: Removal efficiency of dye from aqueous solution at different dye concentrations (pH =7, amount of soil= 1 g, contact time = 30 min).

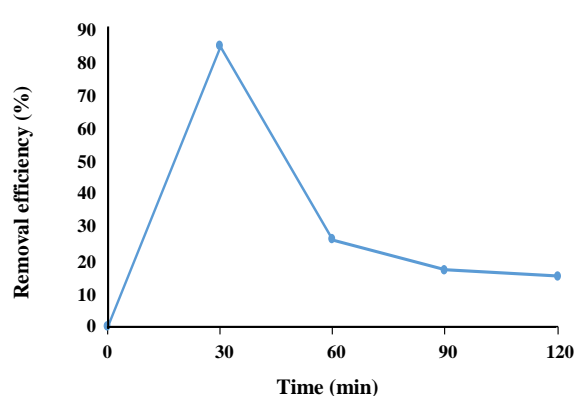


Fig. 4: Removal efficiency of dye from aqueous solution at different contact times (pH =7, dye concentration= 50mg/L, amount of soil = 1 g).

the amount of adsorbed DR 81 decreased due to the fact that fixed dye concentration (50 mg/L) led to the unsaturated active sites on the adsorbate surface and increase in the adsorbate concentrations caused particle aggregation [16]. Similar results were observed in *Gulnaz's* research [16].

Effect of contact time

Fig. 4 shows the percentage removal of DR81 at different contact times ranging from 30 to 120 min. According to Fig. 4, as contact time increased, the removal rate decreased. The maximum removal efficiency (84%) was observed in the 30th min and, thereafter, the rate of adsorption decreased. Rapid adsorption at the initial contact time can be explained by the availability of a positively charged surface of adsorbent that led to the fast electrostatic attraction of the anionic DR81 from the solution [11, 25].

Removal efficiency first increased in the 30th min and then started to decrease with increasing shaking time. The decrease in removal rate for dye might be attributed to the degrading buffer ability in the soil with pH 7, which desorbed the bulky dye molecules and only allows small solvent molecules to enter the soil [23].

Similar [23] and inverse [24, 25] results have been reported in other works.

CONCLUSIONS

Among the various materials that are low cost and easily available, soil containing iron has good properties for adsorption. Experimental data showed that adsorption depended on pH, adsorbent mass, initial dye concentration, and contact time, thus, removal of dye was decreased with increasing reaction time. The optimal conditions

for the removal of dye in the aqueous phase using soil containing iron were as follows: pH= 7, initial dye concentration=50 mg/L, soil amount=1 g and reaction time=30 min, respectively. The economical aspects were considered for selecting the optimal conditions. Therefore, adsorption process using soil is an efficient, reliable, flexible, and cost-effective method for removing Direct Red 81 dye from industrial wastewater.

Nomenclatures

DR 81	Direct Red 81
OC	Organic matter Content
CEC	Cation-Exchange Capacity
EC	Electrical Conductivity
Min	Minute

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