



## Removal of Direct Red 81 dye from aqueous solution using neutral soil containing copper

Mansoorah Dehghani, Marziyeh Ansari Shiri, Samaneh Shahsavani, Narges Shamsedini, Majid Nozari\*

Research Center for Health Sciences, Department of Environmental Health, School of Health, Shiraz University of Medical Sciences, Shiraz, Iran, Tel./Fax: +98 7137260225; emails: dpt2301243389@sums.ac.ir (M. Nozari), mdehghany@sums.ac.ir (M. Dehghani), marziyehansari566@gmail.com (M. Ansari Shiri), shahsavani.samaneh.1989@gmail.com (S. Shahsavani), shams8587@yahoo.com (N. Shamsedini)

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### ABSTRACT

The adsorption efficiency (%) of Direct Red 81 (DR 81) dye using neutral soil containing copper (NSCC) was studied in a batch reactor with respect to adsorbent dose, initial dye concentration, pH and contact time. Maximum adsorption efficiency (41.84%) was obtained from an adsorbent dose of 2 g/L, pH of 3, an initial dye concentration of 50 mg/L and a contact time of 60 min. An increase in the dye adsorption efficiency (%) was observed when the adsorbent dose increased and the pH decreased. The Langmuir and Freundlich isotherm models were tested, and it was found that the Langmuir model was fitted better than the Freundlich model. In addition, the rates of adsorption were found to conform to pseudo-second-order kinetics with good correlation ( $R^2 \geq 0.99$ ). The highest adsorbent recovery (85%) was found with the use of 0.1 M NaOH. The results show that NSCC may be a suitable adsorbent for removal of DR 81 dye due to its low cost and relatively high efficiency.

*Keywords:* DR 81 dye; Adsorption; Soil; Copper

### 1. Introduction

Environmental pollution by industrial wastes is a very important concern due to toxicity and the danger it poses to human health and the environment [1]. Textile industry effluent containing dye causes great damage to the ecological system, polluting many water resources as well. It has also been reported that some dyes may cause allergies, irritation and cancer in humans [2]. Dyes are responsible for waterborne diseases with symptoms such as hemorrhage, nausea, dermatitis, ulceration of the skin and mucous membranes, kidney damage, and a loss of bone marrow leading to anemia [3].

Currently, there are nearly 10,000 different types of commercial dyes and pigments, and over  $7 \times 10^5$  tons of synthetic

dyes are produced annually worldwide [4]. It is estimated that 10%–15% of the dyes are lost in the textile effluent during the dyeing process. Major problems associated with the coloured effluent include decreased light penetration, reduced photosynthesis in plants and damage to the aesthetic nature of the water surface [5–7]. It is difficult to treat dye effluents because of their synthetic origins and their primarily aromatic structures, which are biologically non-degradable [8].

However, conventional wastewater treatment systems (coagulation, flocculation, and biodegradation) used to remove dyes have drawbacks, including high sludge production, handling and disposal problems, slow processing and the need to create an optimally natural environment, as well as maintenance and nutrition requirements. Due to their high costs and disposal problems, many conventional methods for treating dye wastewater have not been widely applied on a large scale in the textile and paper industries [9].

\* Corresponding author.

While various dyes are used in many industries, the textile industry has the highest use of dyes, which are applied to colour fibres [10]. Azo dyes, which constitute 60%–70% of all the dyes produced, are the largest group of dyes in the textile industry; they are used extensively because of their chemical stability and versatility [11]. Many different types of azo dyes (direct, acidic, basic, disperse, reactive, sulfur dyes, the metal complex and mordant) contain carcinogenic aromatic amines. Azo dyes containing  $-N=N-$  are the types most often used [12,13].

In general, various methods, such as photochemical oxidation, nanofiltration and ultrafiltration, ozonation, reverse osmosis, chemical coagulation, electrochemical degradation, integrated chemical/biological degradation and solar photo-Fenton, are used to remove the dyes from industrial wastewater [14,15]. High cost, formation of hazardous by-products, and high energy requirements are the factors that limit the use of these removal methods.

Adsorption under controlled conditions is one of the most effective methods for removing recalcitrant organic pollutants from an aquatic environment [16]. Various adsorbents, such as activated carbon [17,18], sepiolite [19], vermiculite [20] and carbon nanotube [21], are used to remove the dyes from aqueous solution. Activated carbon is the most widely used adsorbent to remove the pollutants from water [17,22,23]. The use of activated carbon is limited by its high cost. Therefore, the application of low-cost adsorbents, such as wood, ash, straw, pug and orange peels, has been reported [24]. Gulnaz et al. [25] demonstrated that the maximum removal efficiency of reactive red 198 dye from aqueous solution by *Potamogeton crispus* was 44.2 mg/g. In addition, one study showed that decolourisation of Direct Red 80 dye by mixing it with different amounts of almond shells was 97% [2].

There are many advantages in using an adsorption system for water contamination control. An adsorption system provides good removal performance, requires less investment in terms of initial cost, more flexible than conventional biological process treatment methods, easier to design and operate than conventional methods and not sensitive to toxic contaminants [26,27]. It is difficult to find affordable and easily provided natural adsorbents that are compatible with the natural environment. Given that iron compounds are known to be a good adsorbent for removal of dyes [28,29], this study's hypothesis posits that copper compounds may also be a good adsorbent for that purpose. Many studies have been conducted on the removal of dyes using adsorption. However, to date, no studies have investigated the application of neutral soil containing copper (NSCC) for the removal of DR 81 dye. There is also a concern that dyes contaminate water resources and have a negative effect on people's health and the environment. The present study aimed to present the use of NSCC to remove DR 81 dye from aqueous solution. To obtain a better understanding of the adsorption mechanisms, the kinetics of dye removal were studied in a batch system. In addition, the effects of different parameters, such as adsorbent dose, initial dye concentration, pH and contact time, on dye removal efficiency were investigated. DR 81 dye was selected in this study as an azo-based dye model, which has been widely used in many industries.

## 2. Materials and methods

### 2.1. Chemicals and equipment

DR 81 dye was obtained from Sigma-Aldrich (USA) and NaOH and HCl were obtained from Merck (Mumbai, India). The chemical structure of DR 81 dye is shown in Fig. 1. A UV-visible spectrophotometer (LAMBDA 750 UV/Vis/NIR Spectrophotometer, PerkinElmer, USA) was used to determine the concentration of DR 81 dye at 508 nm  $\lambda_{max}$ . The stock solution of DR 81 dye (1,000 mg/L) was prepared in double distilled water, and then further diluted to various low concentration solutions. pH was recorded using a pH meter (model 611, Orion Research Inc., USA). X-ray powder diffraction (XRD) analysis was carried out using the PW 1830 apparatus (PANalytical) with monochromated  $CuK_{\alpha 1}$  radiation. The infrared spectra were recorded using a Fourier transform infrared spectrometer (LAMBDA XLS+ Spectrometer, Perkin Elmer 3A, USA). DR 81 dye residual concentrations in soil samples were determined according to the standard method No. 2120 [30].

### 2.2. Soil chemical composition and characteristics

XRD analysis was used to determine the chemical composition of the soil, which was as follows:  $SO_4^{2-}$ ,  $Cl^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , Zn, Cu, Mn, Fe and Pb [31]. A hydrometer was used to determine the soil texture using the Guelph Permeameter method. In addition, soil characteristics such as soil solution, pH [32], organic matter content (OC) [33], cation exchange capacity (CEC) [34], electrical conductivity (EC) [35] and the distribution of particles (%) were determined.

### 2.3. Soil sampling procedure

Soil samples were collected with a hand-driven soil auger at a depth of 0–30 cm from a region close to the Sarcheshmeh Copper Complex, which is located 65 km southwest of Kerman, Iran. The soil samples were transported to the laboratory in zipped plastic bags and kept frozen at  $-20^\circ C$  for 24 h until they were ready for analysis. The soil samples were thawed and air-dried in the dark at room temperature, and they were passed through a 2.0-mm sieve to maintain the homogeneity of the soil and reduce the variability of adsorption data. Then, the samples were put into an oven (Model DHG-9000, Zhengzhou Protech Technology Co., Ltd., China) at  $104^\circ C$  for 2 h until constant weight was reached. Afterwards, the samples were stored in desiccators (Oberoi Plain Desiccator with Lid, Tolexo, India) for further analysis.

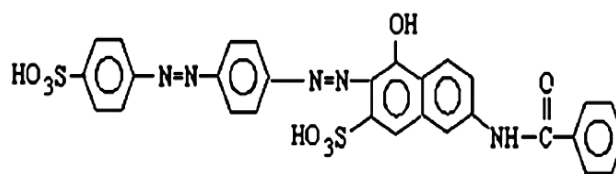


Fig. 1. The chemical structure of DR 81 dye.

#### 2.4. Experimental setup

The effects of operating parameters such as pH (3, 4, 5, 6, 7, 8, 9, 10 and 11), NSCC dose (0.5, 1, 1.5, 2 and 2.5 g/L), initial dye concentration (10, 30, 50, 100 and 150 mg/L) and contact time (5, 10, 15, 20, 25, 30, 60, 90 and 120 min) were studied. The total number of study samples was 75, and the results were presented based on the average of a total number of samples.

The adsorption experiments were carried out in triplicate in the batch reactor. At first, the pH was adjusted with HCl and NaOH. Then, 100 mL of the dye solution was added to the soil samples, which were shaken in a reciprocal shaker at 250 rpm. The samples were centrifuged at 300 rpm for 10 min and then filtered through a grade 4 Whatman filter paper with a pore size of 20–25 μm. After filtration, the residual dye solutions were collected, transferred to a 15-mL glass vial, and stored in a refrigerator prior to spectrophotometric analysis. Through this method of extraction, the percentage of dye recovery from the soil was 98%. The removal efficiency was determined according to Eq. (1) [36]:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

in this equation,  $C_0$  and  $C_e$  are the initial and final dye concentration after adsorption, respectively.

Adsorption kinetics investigations were carried out by stirring 100 mL of DR 81 dye solution in a known initial concentration (0.5 g/L) of adsorbent at a known temperature of  $22^\circ\text{C} \pm 2^\circ\text{C}$  at a pH of  $6.0 \pm 0.2$  at 120 rpm for different time intervals. The amount of dye adsorbed into the NSCC adsorbent at equilibrium,  $q_e$  (mg/g), was calculated by Eq. (2):

$$q_e = \frac{(C_0 - C_e) \times V}{W} \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium dye concentrations in mg/L, respectively;  $V$  is the volume of solution (L) and  $W$  is the mass of the NSCC adsorbent (g). The amount of adsorption at time  $t$ ,  $q_t$  (mg/g), was calculated by Eq. (3):

$$q_t = \frac{(C_0 - C_t) \times V}{W} \quad (3)$$

where  $C_0$  and  $C_t$  (mg/L) are the liquid phase concentrations of the dye at the initial stage and at any time  $t$ , respectively.  $V$  is the volume of solution (L) and  $W$  is the mass of the NSCC adsorbent (g).

The pH at the point of zero charge ( $\text{pH}_{\text{pZC}}$ ) of the adsorbent was measured using the pH drift method described by Kikuchi et al. [37]. The  $\text{pH}_{\text{pZC}}$  of NSCC was determined by adding 0.5 g of NSCC to aqueous 0.1 M  $\text{KNO}_3$  solutions. The pH of the solutions was adjusted to successive initial values between 3 and 11 with either 0.1 M  $\text{HNO}_3$  or 0.1 M  $\text{KOH}$ . The suspensions were stirred at 120 rpm for 48 h, and the final pH was measured and plotted in comparison to the initial pH. The  $\text{pH}_{\text{pZC}}$  is the value at which the final pH is equal to the initial pH.

#### 2.5. Desorption study

Various regeneration methods have been used with different degrees of success. These methods include solvent washing, thermal, chemical and electrochemical regeneration. In this study, desorption of NSCC was studied using six types of solvent media including tap water, distilled water, 0.05 M  $\text{H}_2\text{SO}_4$ , 0.1 M  $\text{HCl}$ , 0.1 M  $\text{HNO}_3$  and 0.1 M  $\text{NaOH}$ . For this purpose, 0.5 g of NSCC was poured in 100 mL of the above mentioned medium and shaken at 120 rpm for 24 h.

#### 2.6. Statistical analysis

Data analysis was conducted using the SPSS Statistical Software Package, version 19.0. The relationship between the operating parameters and the adsorption efficiency (%) was determined using multiple linear regression analysis.  $p$  values less than 0.05 were considered statistically significant.

### 3. Results and discussion

#### 3.1. Soil chemical composition and characteristics

The soil characteristics and chemical composition are presented in Tables 1 and 2. The soil sampling depth, pH (1:1 w/v soil-to-distilled water ratio), EC, OC and CEC were 0–30 cm, 7.8, 1.22  $\text{dSm}^{-1}$ , 0.63% and 10  $\text{cmol/kg}$ , respectively.

Table 1  
Characteristics of the soil investigated

Soil depth (cm)	0–30
CEC (cmol/kg soil)	10
pH	7.8
EC ( $\text{dSm}^{-1}$ )	1.22
OC (%)	0.63
Particles distribution (%)	
Sand	58.0
Silt	26.0
Clay	16.0
Texture	Sandy

Table 2  
The chemical composition of the soil investigated

$\text{SO}_4^{2-}$ (meq/L)	0.9
$\text{Cl}^-$ (meq/L)	6.8
$\text{HCO}_3^-$ (meq/L)	5.2
$\text{CO}_3^{2-}$ (meq/L)	0.0
$\text{Na}^+$ (meq/L)	2.5
$\text{Ca}^{2+}$ (meq/L)	4.8
$\text{Mg}^{2+}$ (meq/L)	5.6
Zn (ppm)	1.48
Cu (ppm)	1.52
Mn (ppm)	5.52
Fe (ppm)	1.9
Pb (ppm)	0.27

The soil texture was sandy. Regarding the soil texture, it should be noted that the sandy content did not have a significant effect on adsorption. The soil copper content was 1.52 mg/kg.

### 3.2. Adsorption kinetic modeling

Studying adsorption kinetics is important because both the rate of adsorption (which is one of the criteria for the efficiency of the adsorbent) and the mechanism of adsorption can result from such studies. In order to analyse the adsorption kinetics of DR 81 dye by NSCC, the pseudo-first-order [38] and pseudo-second-order [39] models were tested. A simple kinetic analysis of adsorption (pseudo-first-order equation) is in the following form:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \quad (4)$$

A pseudo-second-order equation based on adsorption equilibrium capacity may be expressed as follows:

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

where  $q_e$  is the amount of dye adsorbed at equilibrium (g/mg), and  $q_t$  is the amount of dye (mg/g) adsorbed at  $t$  time;  $k_1$  is the rate constant of the pseudo-first-order model (1/min), and  $k_2$  is the rate constant of the pseudo-second-order model (g/mg min). The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients ( $R^2$ ).

A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of the dye adsorption. As seen in Table 3, these results demonstrate that the experimental data do not agree with the pseudo-first-order kinetic model. The rates of adsorption were found to conform to pseudo-second-order kinetics with good correlation ( $R^2 \geq 0.99$ ). Fig. 2 and 3 show the pseudo-first-order and pseudo-second-order curve-fitting plots.

### 3.3. Adsorption isotherms

In this work, the Langmuir and Freundlich models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration [1]. The applicability of the isotherm equations was compared by

investigating the correlation coefficients,  $R^2$ . The Langmuir equation is commonly expressed as [40]:

$$\left(\frac{c_e}{q_e}\right) = \frac{1}{q_m K_L} + \left(\frac{C_e}{q_m}\right) \quad (6)$$

where  $q_m$  is the maximum amount of adsorption (mg/g),  $K_L$  is the affinity constant (L/mg) and  $C_e$  is the solution concentration at equilibrium (mg/L). The maximum adsorption capacity and Langmuir constant were calculated from the slope and intercept of the linear plots  $C_e/q_e$  vs.  $C_e$  which gives a straight line of slope  $1/q_m$ , which corresponds to complete monolayer coverage (mg/g) and the intercept  $1/q_m K_L$ .

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems [1]. The Freundlich isotherm is given in logarithmic form as [40]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

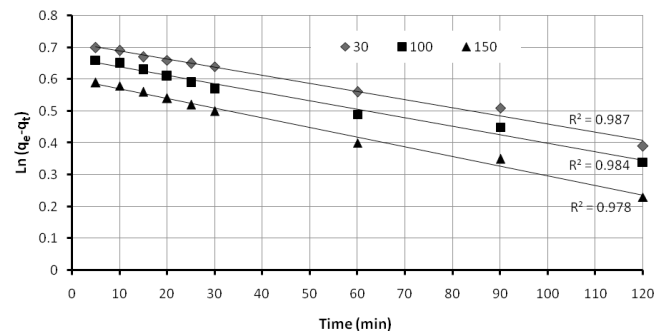


Fig. 2. Pseudo-first-order kinetic plots for DR 81 dye adsorption (concentrations of 30, 100 and 150 mg/L) on NSCC.

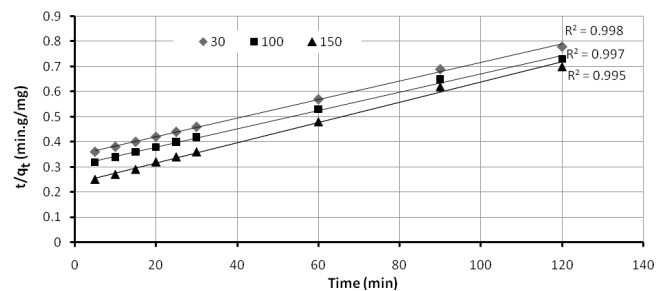


Fig. 3. Pseudo-second-order kinetic plots for DR 81 dye adsorption (concentrations of 30, 100 and 150 mg/L) on NSCC.

Table 3  
Comparison of the pseudo-first-order and pseudo-second-order adsorption constants

Pseudo-first-order			Pseudo-second-order			Temperature (°C)	Concentration of Direct Red 81 dye (mg/L)
$k_1$ (1/min)	$R^2$	$q_e$ (g/mg)	$k_2$ (g/mg min)	$R^2$	$q_e$ (g/mg)		
0.123	0.987	11.34	0.016	0.998	21.61	22 ± 2	30
0.13	0.984	17.49	0.025	0.997	17.69		100
0.143	0.978	19.12	0.06	0.995	13.81		150

where  $k_f$  (mg/g) and  $n$  are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.  $k_f$  and  $n$  can be determined from the linear plot of  $\log q_e$  vs.  $\log C_e$ . Adsorption isotherms were obtained from Eqs. (6) and (7) using the experimental adsorption results from these equations. The values  $q_m$ ,  $K_L$ ,  $k_f$ ,  $R^2$  and  $n$  are summarised in Table 4. By comparing the results presented in Table 4, it is clear that the correlation coefficient of the Langmuir model is higher than that of the Freundlich model, which means that the Langmuir adsorption isotherm more accurately describes DR 81 dye adsorption on NSCC. The fact that the Langmuir isotherm fits the experimental data very well may confirm the monolayer coverage of the dye onto NSCC particles and also the homogeneous distribution of active sites on the adsorbent since the Langmuir equation assumes that the surface is homogeneous.

3.4. Desorption performance

Desorption of a dye or regeneration of an adsorbent from a used adsorbent is crucial for repeating the use of an adsorbent, recovering the dye and reducing the cost of operation in any treatment system. Six solvents were used for the desorption/regeneration experiment, and the results are presented in Fig. 4. Among the solvents, the use of tap water, distilled water and 0.1 M HNO<sub>3</sub> resulted in a limited amount of dye recovery (<40%). The highest (85%) dye recovery was found with the use of 0.1 M NaOH. The other two acids, 0.1 M HCl and 0.05 M H<sub>2</sub>SO<sub>4</sub>, had lower efficiencies (54% and 52%, respectively). The recovery and reuse processes for NSCC can be continued up to five times with minor deviation in removal efficiency.

3.5. Effect of pH

The results of the present study demonstrated that the maximum adsorption efficiency (32.03%) for DR 81 dye was achieved in an acidic range (pH = 3). However, in basic pH levels (pH = 11), the adsorption efficiency (%) of DR 81 dye in the aqueous phase decreased to 4.68% (Fig. 5). Multiple linear regression analysis showed that there was a significant difference between pH and the adsorption efficiency (%) of DR 81 dye ( $p < 0.001$ ). Controlling for pH is usually a significant factor in the adsorption process [1,35]. The pH of the system influenced the adsorption efficiency (%) due to its effect on the surface properties of the adsorbent, the ionisation of the adsorbed molecule and the electrostatic force of attraction during the adsorption process [41]. Therefore, the interaction between the dye (DR 81 dye) and the adsorbent (NSCC) is mainly affected by the ionisation states of the functional groups on both the dye molecule and the adsorbent surface [42]. The  $pH_{PZC}$  of the surface of an adsorbent is important because it indicates the net surface charge of the NSCC in

solution. The experimental results of the  $pH_{PZC}$  determination are presented in Fig. 6. As seen, the  $pH_{PZC}$  of NSCC is

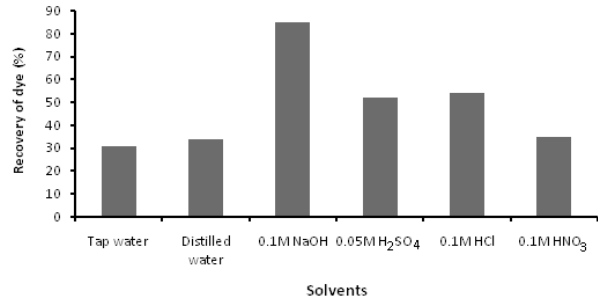


Fig. 4. Desorption of DR 81 dye from NSCC (dye concentration: 50 mg/L; desorption time: 24 h and temperature: 20°C).

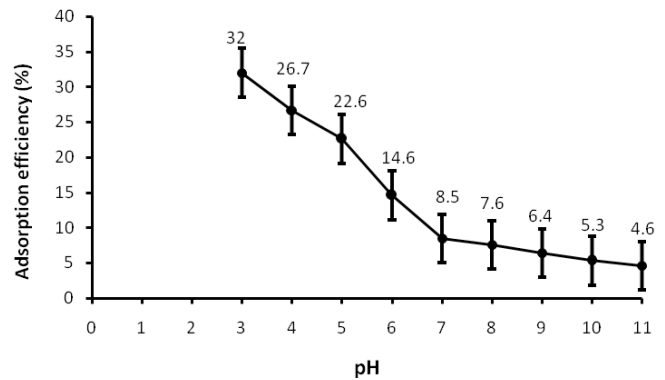


Fig. 5. Effect of pH on the adsorption efficiency (%) of DR 81 dye from aqueous solution using NSCC (initial dye concentration, 50 mg/L; adsorbent dose, 1 g/L and contact time, 30 min).

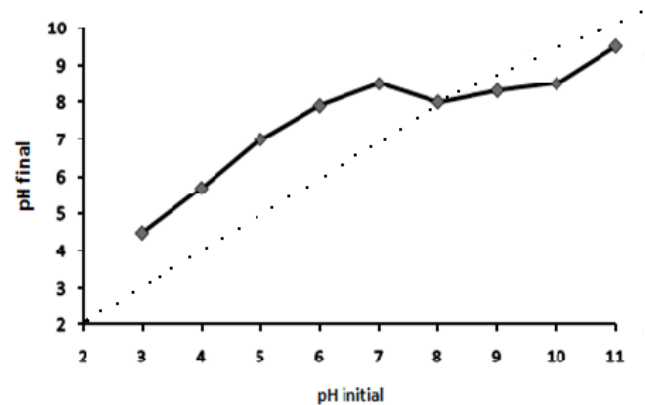


Fig. 6.  $pH_{PZC}$  of the NSCC, determined using the pH drift method.

Table 4  
The Langmuir and Freundlich constants for DR 81 dye adsorption on NSCC

Langmuir isotherm			Freundlich isotherm			Temperature (°C)	Type of adsorbent
$K_L$ (L/mg)	$q_m$ (mg/g)	$R^2$	$k_f$ (mg/g)	$n$	$R^2$		
3	26.2	0.99	1	1.1603	0.97	22 ± 2	NSCC

at pH 8. This means that there were positively charged ions on the NSCC surface. When the solution pH was lower than  $pH_{pzc}$ , the amount of dye removal was relatively high, possibly due to the presence of more positive charges on the NSCC surface. When the solution pH was higher than  $pH_{pzc}$ , the amount of dye removed decreased possibly due to the increasing negative charges and the decreasing positive charges on the NSCC. A negatively charged surface site on the soil is not favorable for the adsorption of anionic direct red molecules due to the electrostatic repulsion [41]. Similar results have been observed for the adsorption of Direct Blue 71 from aqueous solution via wheat shells [1,24,41,43]. However, the results reported by Tahir and Rauf [44] were completely different from our findings. They concluded that the adsorption efficiency of the dye increased at a higher pH due to the abundance of  $OH^-$  ions and the electrostatic repelling forces among the negative charge surfaces and the dye anionic molecules [44].

### 3.6. Effect of initial DR 81 dye concentrations

The dye adsorption efficiency (%) increased from 26.23% to 32.03% as the initial dye concentration increased from 10 to 50 mg/L. After that, the adsorption efficiency (%) significantly decreased (10.01%) by increasing the initial dye concentration (50–100 mg/L) (Fig. 7). Multiple linear regression analysis showed that there was a significant difference between the initial dye concentration and the DR 81 dye adsorption removal amount ( $p < 0.005$ ). The initial increase in DR 81 dye adsorption efficiency (%) can be attributed to the abundant vacancy sites in the initial phase [45]. In addition, the dye adsorption efficiency (%) decreased from 32.03% to 22.02% as the initial DR 81 dye concentration increased from 50 to 150 mg/L. This result demonstrates that as more sites in the soil were filled, it became increasingly difficult for the DR 81 dye molecules to find a vacant site [46–49]. The results reported by Bayramoğlu and Arıca [41] are similar to those of the present study. Moreover, other studies have reported the adverse results that were found in the present study [1,46].

### 3.7. Effect of adsorbent dosage

DR 81 dye adsorption efficiency (%) for different adsorbent doses was in the range of 22.56% to 40.49% (Fig. 8). Multiple linear regression analysis showed that there was a significant difference between the adsorbent dose and the DR 81 dye adsorption efficiency (%) ( $p < 0.005$ ). By increasing the adsorbent dose (NSCC) (0.5–2 g/L), the DR 81 dye adsorption efficiency (%) increased (17.93%); afterwards, the dye adsorption efficiency (%) decreased by increasing the amount of NSCC (Fig. 8). The maximum adsorption efficiency (%) (40.49%) was achieved at 2 g/L of NSCC, contact time = 30 min, pH = 3, and initial DR 81 dye concentration = 50 mg/L. At first, increasing the DR 81 dye adsorption efficiency (%) with adsorbent dose (NSCC) can be attributed to increasing NSCC surface area and availability of more adsorption sites [16,50]; but afterwards, the decrease of the DR 81 dye adsorption efficiency (%) can be attributed to the fact that the fixed dye concentration (50 mg/L) led to unsaturated active site on the adsorbent surface (NSCC) [14,46,51]. The results reported by Gulnaz et al. [25] are similar to those of the present study.

### 3.8. Effect of contact times

The maximum DR 81 dye adsorption efficiency (41.84%) was observed at 60 min and, thereafter, the adsorption efficiency (%) decreased (Fig. 9). Multiple linear regression analysis also showed that there was a significant difference between the contact time and DR 81 dye adsorption rate ( $p < 0.005$ ). Rapid adsorption at the initial contact time can be explained by the availability of positively charged surface of

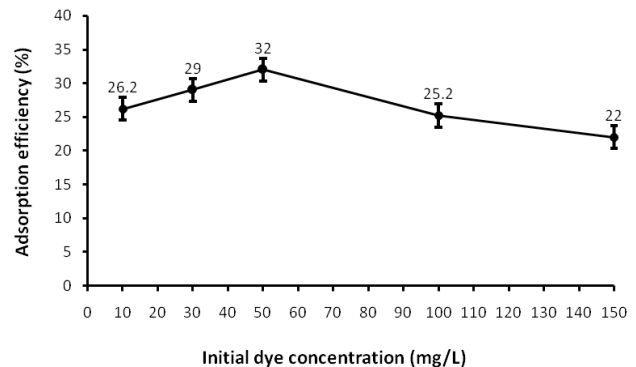


Fig. 7. Effect of initial dye concentrations on the adsorption efficiency (%) of DR 81 dye from aqueous solution using NSCC (pH, 3; adsorbent dose, 1 g/L and contact time, 30 min).

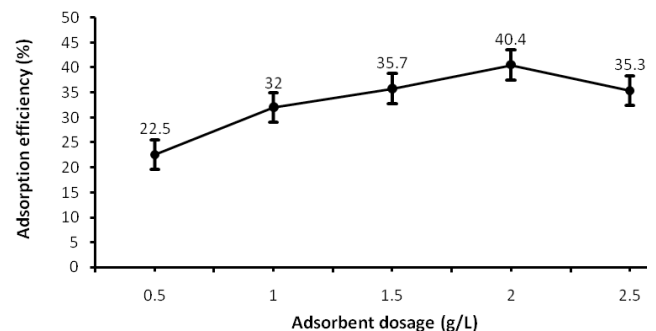


Fig. 8. Effect of adsorbent (NSCC) doses on the adsorption efficiency (%) of DR 81 dye from aqueous solution using NSCC (pH, 3; initial dye concentration, 50 mg/L and contact time, 30 min).

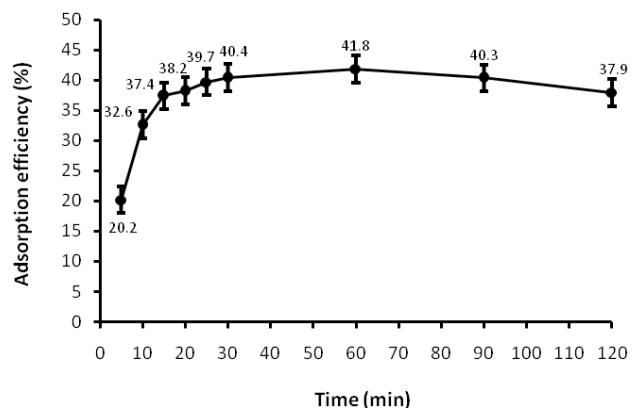


Fig. 9. Effect of contact times on the adsorption efficiency (%) of DR 81 dye from aqueous solution using NSCC (pH, 3; initial dye concentration, 50 mg/L and adsorbent dose, 2 g/L).

the adsorbent that led to the fast electrostatic attraction of the anionic DR 81 dye from the solution [16,49,50]. In this study, at first, adsorption efficiency (%) increased at 60 min and then started to decrease with increasing the contact time. The results reported by Tahir and Rauf [44] are similar to the present study findings. However, other studies have reported the adverse results that were found in the present study [16,42,50] due to using adsorbents with different capacities.

### 3.9. Effect of copper

The sulfate content  $\text{SO}_4^-$  in the soil can be reduced to  $\text{SO}_3^{2-}$ . Then, sulfite may react with Cu and generate reactive peroxy radical [52]. Advanced oxidation processes (AOPs) might be effective in removing DR 81 dye through sulfite/Cu process. Therefore, it can be suggested that the used soil in this study might have removed the DR 81 dye by both adsorption and AOPs.

## 4. Conclusion

The NSCC used as the adsorbent for DR 81 dye had a  $\text{pH}_{\text{PZC}}$  of 8.0. Two models were applied to describe the kinetics of dye adsorption. The best fit for the kinetic data was obtained with the pseudo-second-order model. Two isotherm models were applied to the experimental equilibrium data, with the Langmuir model giving the best fits. The adsorption of the dye on the NSCC increased as the adsorbent dosage increased and the pH decreased. The highest adsorbent recovery (85%) was found with the use of 0.1 M NaOH. The mean removed amount of dye by adsorption batch experiment in aqueous solution with NSCC was up to 41%. Based on the data of the present investigation, one could conclude that the NSCC being a natural, eco-friendly and low-cost adsorbent with relatively large adsorption efficiency might be a suitable local alternative for elimination of dyes from the coloured aqueous solutions.

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