



Adsorption of Acid Yellow-73 and Direct Violet-51 Dyes from Textile Wastewater by Using Iron Doped Corncob Charcoal

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Abstract

The presence of synthetic dyes in textile industry wastewater lead to deterioration of precious fresh water resources, making the need to remove dyes crucial for environmental protection. Recently, different techniques have been employed to remove these dyes from water resources. Among them, biosorption has gained tremendous popularity due to its eco-friendly nature and inexpensive method. In this study, the removal potential of two acid dyes, i.e. yellow-73 and direct violet-51, was assessed from textile effluent samples using iron modified corncob charcoal. The adsorption efficiency ranged between 93.93 - 97.96 % and 92.2 - 95.4 % for acid yellow-73 and direct violet-51, respectively. Furthermore, study highlights optimum parameters for successful adsorption of these dyes, such as stirring time (numbers), pH (numbers), temperature (numbers), and adsorbent dosage (numbers). Keeping in consideration these findings, we recommend the use of Iron Doped Corncob Charcoal (IDCC) as a low-cost, efficient alternative for wastewater treatment, primarily minimizing the detrimental effects of hazardous dyes.

Keywords: Acid Yellow-73; Adsorption; Corncob; Direct Violet-51; Textile Wastewater.

Introduction

Water is essential for life. In total, approximately 3% fresh water is available on earth comprising < 1% for human consumption [1]. With rapid population explosion, urbanization, and advancements in technology, water resources have been drastically deteriorated as a result of direct discharge of untreated wastewater into the surface water streams [2]. Among different pollution sources, wastewater coming out of the textile industry containing harmful chemicals including synthetic dyes, is a serious concern. These chemicals have been found to severely deteriorate the surface water quality [3,4], and groundwater

resources [5], ultimately posing a serious threat to human and animal life [6].

In Pakistan, textile industry is backbone of the country's economy, accounting for 9% of the total gross national product (GNP) [7]. The adsorption of dye from textile wastewater can be performed by chemical, biological and/or physical treatment methods [8]. However, due to high operation cost and lower efficacy, most of these methods are deemed inefficient. In recent years, biosorption is gaining increasing acceptance due to process simplicity, cost effectiveness and higher

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efficiency [4, 9]. As a principle, biosorption involves entrapment of dyes in the matrix of the adsorbent without destruction of the pollutant [9].

Many researchers have reported the use of agricultural biomass as a biosorbent [10]. Due to their inexpensive nature and higher availability in agricultural countries like Pakistan, adsorbents are being produced in large quantities, even fronting disposal issues [11]. Therefore, their usage as biosorbent may help scientists reduce wastewater contamination. Among different agricultural adsorbents, corncob (central core of maize ear) has been reported as an efficient biosorbent [12] with high biomass production [13]. According to a study, 100 kg of corn grain produce approximately 18 kg of corncob [13]. Therefore, its direct use in dyes removal can bring innovative solution in environmental technologies. Furthermore, necessary modifications in such agricultural by-products may increase the ion-exchange capacity of the adsorbent, resulting in higher removal rates. The present study aims to evaluate the adsorption rates of two azo dyes, i.e. acid yellow-73 and direct violet-51, from aqueous media and industrial wastewater using a modified iron doped corncob charcoal (IDCC). To best of our knowledge, this is first study conducted on this issue primarily assessing the adsorption potential of textile industry dyes.

Materials and Methods

Preparation of biosorbent

Corn cob obtained from a local market, was oven dried at 90 °C. The dried corncob was then grounded using mortar grinding machine leading to burning in an air-tight cauldron until it converted to charcoal with approximate output being 678 g/kg. The charcoal was further grounded into powder form. Then 100g of powdered charcoal was added to a conical flask containing 1000 ml of FeCl₂ solution (1 g/1000 ml) [14]. To this mixture, solution of NaBH₄ (2 g/500 ml) was added drop wise using a dropping funnel over a period of 24 hours along with continuous stirring using a magnetic stirrer. Finally, the suspension was filtered using a filtration assembly and the residue containing iron doped charcoal was then oven-dried for 8 hours at 90 °C and sieved through 300 µm mesh to achieve experimental IDCC.

Sample collection

Wastewater samples were collected from three local textile mills discharging acid yellow-73 and direct violet-51 dyes. All the wastewater samples were collected and preserved in accordance with the guidelines of American Public Health Association [15].

Analytical measurements

In order to check the effect of stirring time, temperature, pH and adsorbent dosage, separate concentrated standard solutions of acid yellow-73 and direct violet-51 dyes were prepared by dissolving 500 ppm of dyes in water.

The dyes concentration in the dye solutions, subsequent to the adsorption process, were confirmed using HACH DR 2800 Spectrophotometer by measuring absorbance at $\lambda_{\text{max}} = 481 \text{ nm}$ and $\lambda_{\text{max}} = 589 \text{ nm}$ respectively. Batch adsorption experiments were performed where one variable was studied at a time while others were kept constant to obtain optimum conditions. A number of parameters were tested such as stirring time, pH, temperature and dosage of adsorbent. Finally, for applying adsorption isotherms, optimum conditions were applied with gradual change in dye concentration up to 1000 ppm.

Results and Discussion

Effect of stirring time

The adsorption efficiency of acid yellow-73 and direct violet-51 on IDCC was ascertained as a function of stirring time (Figure 1a and 1b). Fig. 1a depicts that the adsorption capacity for acid yellow-73 dye initially increases with intensification in the stirring time until maximum adsorption occurs at 60 minutes of constant stirring, followed by a gradual decrease in adsorption capacity. The adsorption of direct violet-51 increases continuously with increase in stirring time, and the maximum adsorption capacity is determined at 120 minutes of constant stirring (Fig. 1b). Therefore, the stirring time adopted for subsequent adsorption analyses of acid yellow-73 and direct violet-51 dyes were 60 and 120 min respectively.

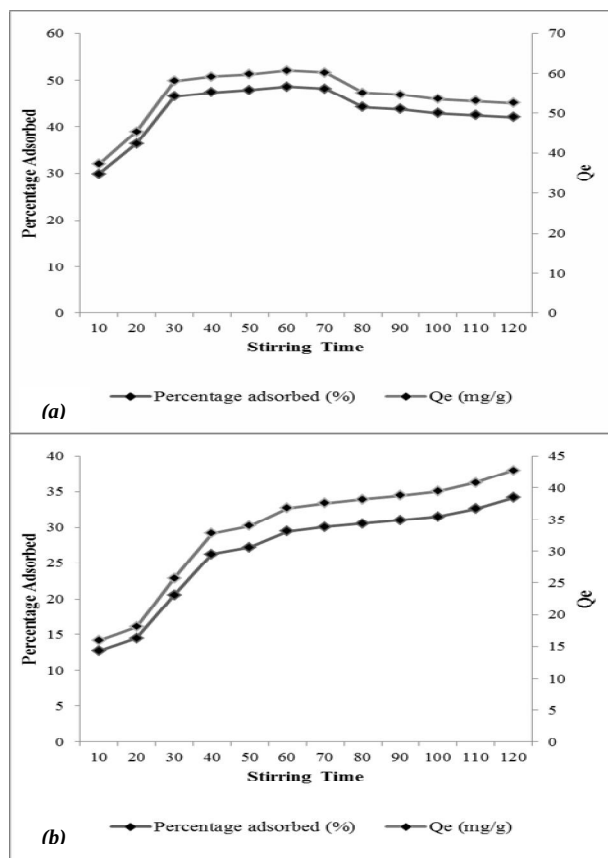


Figure 1. Effect of stirring time (mins) on the percentage adsorption and maximum adsorption capacity of (a) acid yellow-73 and (b) direct violet-51 dyes on IDCC

Effect of pH

The adsorption capacity of adsorbent is the function of pH [5, 12] as their properties are directly altered by hydrogen ion concentration in the dye solution [16]. Many studies have reported the effect of pH on adsorption capability of adsorbent in removal of dyes [12, 16-18]. Results revealed a slight variation in adsorption capacity of the acid yellow-73 on IDCC in the dye solution for the pH ranging from 1 to 12. The maximum adsorption of the acid yellow-73 was observed at pH 3 (Fig. 2a). According to a study conducted by Iqbal *et al.* [17], decrease in adsorption occurs below pH 3 as anions in the solution compete with the anionic dye. Similarly, a minor variation in the adsorption capacity of direct violet-51 dye was observed at pH values ranging from 1 to 12 (Fig. 2b). Therefore, the study indicates that pH is not a limiting factor for the removal of both acid yellow-73 and direct violet-51 dyes using IDCC as biosorbent.

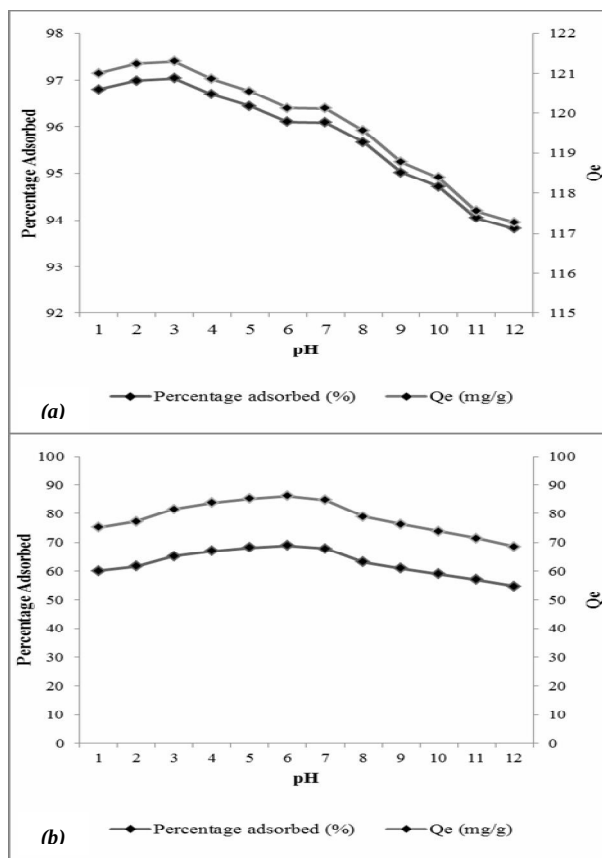


Figure 2. Effect of pH on the percentage adsorption and maximum adsorption capacity of (a) acid yellow-73 and (b) direct violet-51 dyes on IDCC

Effect of temperature

Results on temperature effect elucidates that the adsorption of acid yellow-73 and direct violet-51 dyes on IDCC is dependent upon the temperature of the aqueous media (Fig. 3a and 3b). The rise in temperature stimulates a positive effect on the adsorption of acid yellow-73 dye on IDCC (Fig. 3a). This adsorption process is hence concluded to be endothermic and the increased adsorption with rise in temperature might be attributed to enhanced mobility of the ions at elevated temperature [19]. On the other hand, effect of temperature on adsorption of direct violet-51 dye is conversely shown as a blend response which is in contrast to exothermic adsorption reported by Sadaf *et al.* [20]. The adsorption of direct violet-51 dye has first shown an endothermic adsorption, until it reached maximum adsorption capacity at 70°C (threshold temperature), followed by an exothermic adsorption process (Fig. 3b).

This sudden decrease in adsorption capacity of direct violet-51 dye might be attributed to the degradation of IDCC in the presence of this dye with rise in temperature from threshold point, hindering the adsorption process.

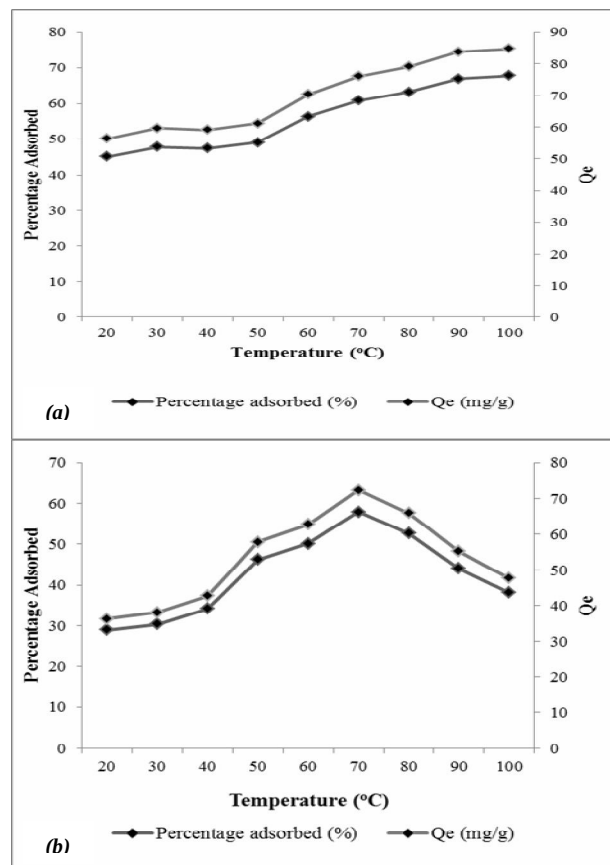


Figure 3. Effect of temperature (°C) on the percentage adsorption and maximum adsorption capacity of (a) acid yellow-73 and (b) direct violet-51 dyes on IDCC

Effect of adsorbent dosage

The adsorbent dosage is found to have significant effect on the adsorption process of dye removal [21]. (Fig. 4a and 4b). It can be inferred from the results that the adsorption efficiency can be improved, up to a certain limit, with the increase in adsorbent dosage. This could be due to the enhancement in the adsorption sites for the dye molecules. More specifically, adsorption of acid yellow-73 dye increased with rise in adsorbent dosage, until a maximum adsorption capacity of 0.15g dose of the adsorbent (Fig. 4a). After this concentration, the adsorption remains constant even with the increase in adsorbent dosage. Similar trend was found in percentage adsorption for direct

violet-51 dye that attained a maximum adsorption capacity of 0.25g of adsorbent dosage (Fig. 4b). Preethi et al. [12] and Demirbas et al. [22] also reported similar findings on increased adsorption by increasing dosage. The difference in optimized dosage for two dyes is dependent upon size fit concept [16] and the doses were considered as optimum for subsequent experimentations.

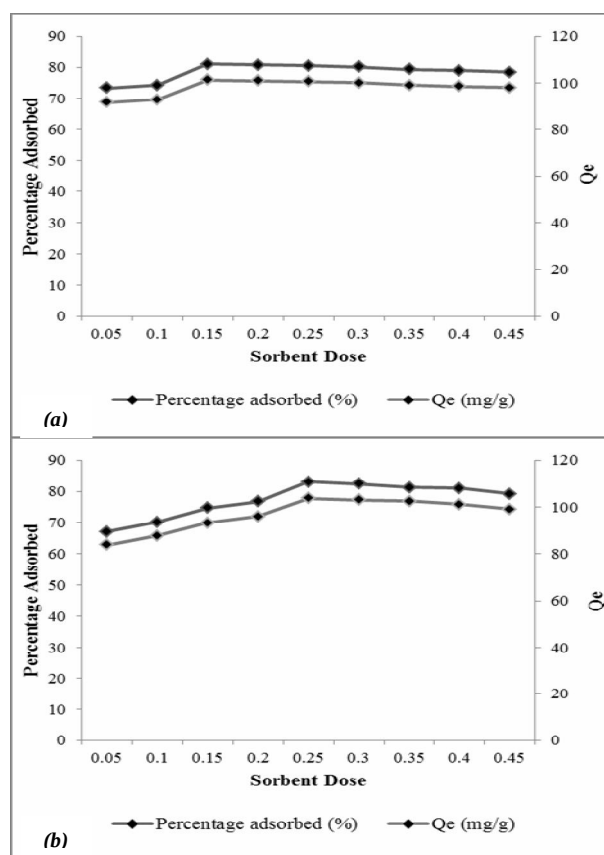


Figure 4. Effect of adsorbent dose on the percentage adsorption and maximum adsorption capacity of (a) acid yellow-73 and (b) direct violet-51 dyes on IDCC

Adsorption isotherms

The adsorption isotherms relating the adsorbate concentration adsorbed on the surface, provide us the capacity of the adsorbent at constant temperature [16]. The Langmuir and Freundlich adsorption isotherms have been used to study the adsorption data of dyes. Their description is provided in the following sections.

Langmuir isotherm

The adsorption data obtained was first analyzed using the linear form of Langmuir

adsorption isotherm where monolayer adsorption is assumed with homogenous sites and no lateral molecular interaction [23]. The Langmuir adsorption isotherm is most commonly used isotherm with standard linear form as given in Eq. (1) [24]:

$$\frac{1}{q_e} = \frac{1}{b \cdot q_m \cdot C_e} + \frac{1}{q_m} \quad (1)$$

Where, q_e and C_e are adsorbed concentration (mg.g^{-1}) and equilibrium concentration ($\mu\text{g.mL}^{-1}$) of the dye, respectively. The values q_m (mg.g^{-1}) and b (L.g^{-1}) are Langmuir isotherm parameters. The value R^2 (correlation coefficient) indicate a good fit of the data with Langmuir model.

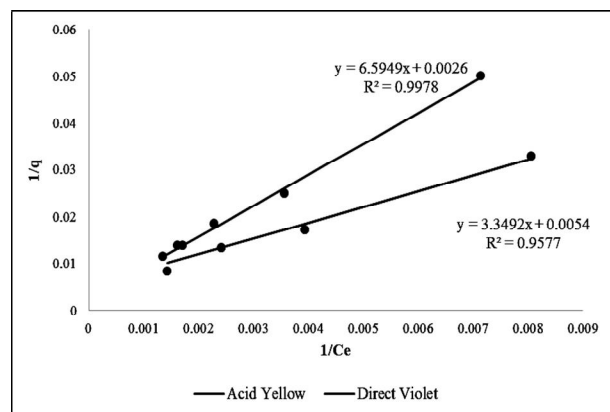


Figure 5. Langmuir isotherm for adsorption of acid yellow-73 and direct violet-51

Both acid yellow-73 and direct violet-51 dyes have shown a strong correlation with Langmuir model with value of R^2 at 0.9978 and 0.9577, respectively (Fig. 5). The maximum adsorption capacity was comparatively higher in acid yellow 73 coinciding with increased dye removal. Therefore, it has been revealed that adsorption of acid yellow-73 and direct violet-51 dyes fit the Langmuir model.

Freundlich isotherm

The adsorption data was also analyzed using the linear form of Freundlich isotherm model as given in Eq. (2)[24]. The Freundlich model assumes multilayer adsorption on a heterogeneous surface [18, 24].

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

Where, q_e is the adsorbed dye concentration (mg.g^{-1}) and C_e is the equilibrium dye concentration (mol L^{-1}). Whereas, K_F and n are Freundlich isotherm parameters.

Similar to Langmuir model, both dyes showed correlation with the Freundlich model, but n value of direct violet-51 (i.e. $n = 1.5$) indicated more affinity towards heterogeneous adsorption as compared to acid yellow-73 ($n = 0.93$) (Fig. 6). Values of $n > 1$ show favorable conditions for heterogeneous adsorption [16]. Maximum adsorption capacity of direct violet-51 was higher than yellow-73, indicating increased removal utilizing multilayer adsorption. Comparison of the correlation coefficients indicated Freundlich Model is better fit for Acid Yellow-73 and Langmuir Model for Direct Violet-51 (Table 1). Applicability of both models demonstrates coexistence of both monolayer and multilayer adsorption depending on experimental conditions [25].

Table 1. Langmuir and freundlich parameters for acid yellow-73 and direct violet-51.

	Langmuir			Freundlich		
	q_m (mg.g^{-1})	b (L.g^{-1})	R^2	n	K_f	R^2
Acid Yellow	384.615	0.00459	0.982	0.927	0.548	0.995
Direct Violet	185.185	0.00824	0.988	1.508	1.325	0.886

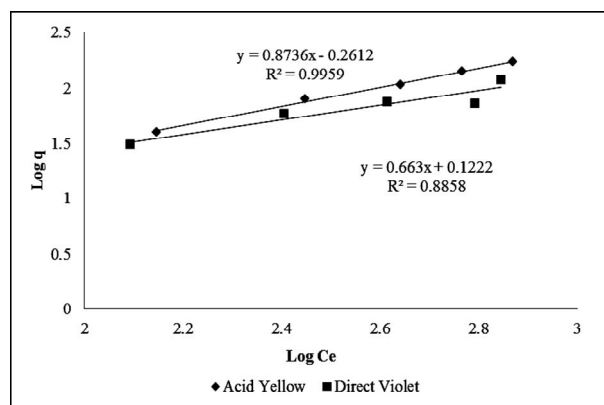


Figure 6. Freundlich isotherm for adsorption of acid yellow-73 and direct violet-51

Thermodynamic parameters

Temperature was observed to be a major factor in adsorption of both dyes. Hence the thermodynamic parameters which provided information regarding the energetic changes accompanying adsorption were observed using the equation:

$$\Delta G^{\circ} = -RT \ln K_c$$

Where ΔG° is Gibbs free energy, R is general gas constant and K_c is equilibrium constant derived as ab ratio of amount of metal adsorbed on unit mass (q) and equilibrium concentration of metal ions (C_e) [27].

The equilibrium constant (K_c) was calculated using the Van't Hoff equation:

$$\ln K_c = \frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

With ΔS° and ΔH° being change in entropy and enthalpy respectively which were determined from slope and intercept of Vant't Hoff's plot of $\ln K_c$ versus $1/T$.

The thermodynamic parameters of Gibbs free energy, entropy and enthalpy change were observed (Table 2). Negative values of ΔG° for acid yellow-73 at all observed temperatures indicated spontaneous and thermodynamically favorable adsorption while positive ΔG° obtained for Direct Violet showed non spontaneous and unfavorable sorption. The low values of ΔG° represented physisorption as the main mechanism for removal of both dyes with weak interactions [27, 28].

The Van't Hoff plot was drawn by observing adsorption while changing the temperature and linear plots were obtained for acid yellow-73 and direct violet-51. The values of ΔS° and ΔH° were 0.0447 KJ.mol⁻¹.K⁻¹ and 11.14 KJ.mol⁻¹ for acid yellow-73 respectively. Positive value of ΔH° along with decreasing ΔG° suggested endothermic mode of adsorption which matched the increased efficiency at higher temperatures, while its small value represented a weak

interaction [29]. Increase in adsorption with temperature maybe due to increased mobility of ions with increasing temperature. The values of ΔS° and ΔH° were 0.0651 KJ.mol⁻¹.K⁻¹ and -18.77 KJ.mol⁻¹ for Direct Violet respectively which indicated exothermic mode of adsorption. Positive change in entropy suggested increase in degree of freedom, thus increased randomness during adsorption of both dyes [28].

Table 2. Thermodynamic parameters calculated for acid yellow-73 and direct violet-51 dyes adsorption.

Dye	Temperature (K)	ΔG° (KJ.mol ⁻¹)	ΔH° (KJ.mol ⁻¹)	ΔS° (KJ.mol ⁻¹ .K ⁻¹)
Acid Yellow	283	-2.18739		
	303	-2.54625		
	323	-3.70925	10.87	0.0439
	343	-4.78623		
Direct Violet	283	0.495064		
	303	1.247984		
	323	3.152333	-18.778	0.06513
	343	3.576858		

Industrial applicability of adsorbent

In order to assess the industrial applicability of IDCC for the removal of acid yellow-73 and direct violet-51 dyes from the wastewater, samples of three different textile industries were selected randomly for subsequent experimentation. The adsorption potential for acid yellow-73 and direct violet-51 dyes in industrial wastewater was assessed at previously optimized stirring time, pH, temperature, and adsorbent dosage. The removal efficiency in all the three wastewater samples ranged between 93.93 - 97.96 % and 92.2 - 95.4 % for acid yellow-73 and direct violet-51 dyes, respectively (Fig. 7a and 7b). Thus, successful biosorption potential of IDCC for removal of acid yellow-73 and direct violet-51 dyes from the industrial wastewater gives us a cheap and efficient method for further research in this field.

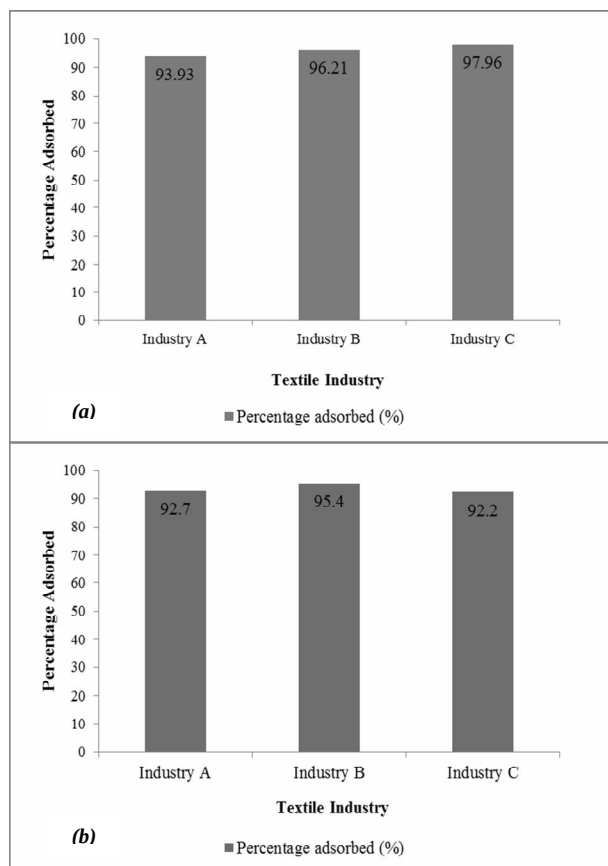


Figure 7. Percentage adsorption of (a) acid yellow-73 and (b) direct violet-51 dyes from textile wastewater on IDCC

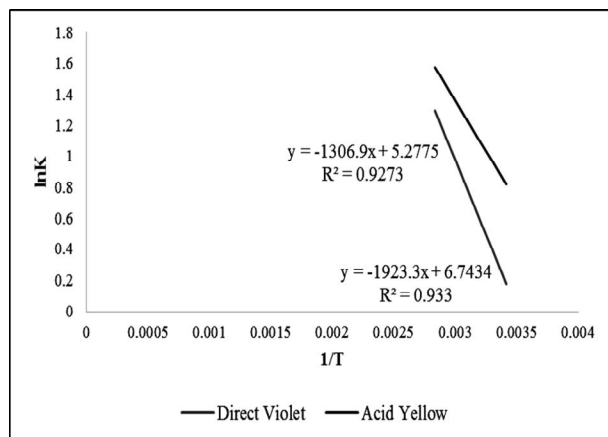


Figure 8. Vant Hoff Plot for acid yellow-73 and direct violet-51 dyes

Conclusions

The present study indicates that the modified corncob with the iron doping could be used as an effective tool for the removal of acid yellow-73 and direct violet-51 dyes from the

textile wastewater. Results revealed that the removal efficiency for acid yellow-73 and direct violet-51 dyes at optimum conditions can be achieved up to 97.96 % and 95.4 % respectively. Therefore, the study may help environmental scientists to employ IDCC in textile industry as a low cost and effective alternative to conventional wastewater treatment processes, minimizing the detrimental effects associated with the discharge of these hazardous dyes into the environment..

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