Removal of Direct Red 16 (Textile Dye) from Industrial Effluent by using Feldspar

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Summary: Dyes are one of the major categories of environmental pollutants. Unfortunately disposal of these hazardous chemical pollutants is usually done by throwing them in any nearby water channels. Physical adsorption is an efficient and cost effective technique to eliminate dyes from waste water. In present study Feldspar is used as adsorbent for the removal of Direct red 16 (textile dye). Different parameters like speed of shaking, adsorbent dosage, time of contact of two phases, pH and analyte concentration were optimized to get maximum adsorption capacity *i.e.* FTIR analysis of adsorbent was done to study the functional groups present on surface of adsorbent. Adsorption isotherms Langmuir and Fruendlich were investigated to evaluate the values of Q and K which were 5.30 mgg^{-1} and 1.25 mgg^{-1} respectively. Values of thermodynamic parameters ΔH (change in enthalpy), ΔS (change in entropy) and ΔG (change in Gibbs energy) were calculated. The results of adsorption indicate that physisorption is much favorable for adsorption of Direct Red 16 on feldspar. So, Feldspar was proven a good adsorbent and found to have good potential for removal of Direct Red 16 from waste water.

Key Words: Adsorption Isotherm, Feldspar, Direct Red 16, Adsorption.

Introduction

Industrial waste water is one of the major problems of modern world. Due to proliferating development of industrial sector the volume of this wastewater is increasing day by day. Therefore, the treatment of industrial effluents is subject of global concern. Presence of dyes in industrial effluents is posing very serious impact on environment and health of biota. Different industries like textile, tanneries, paper & pulp and paints are the major consumers of dyes. Even a small amount of dyes in water bodies causes disastrous effects on human [1], aquatic life [2] and other mammals [3]. Synthetic textile dyes also affect different natural processes in water bodies like biodegradation, photosynthesis, inhibit light penetration and resist biological oxidation [4]. The content of pollution included in the wastewater depends on the type of industry and treatment facilities available there. Various physical, chemical and biological techniques are available for the elimination of hazardous textile dyes from effluents such as precipitation, advance oxidation methods (AOPs), membrane filtration, and electrolytic filtration etc, but either these methods are expensive or time consuming. In contrast adsorption technique is efficient, effective, simple and low cost, that is why it is becoming popular in recent years. A volume of published literature is available in which different low cost adsorbents are introduced for the removal of contaminants from wastewater [5-8].

Geological materials such as sand have already been proven excellent adsorbents for the elimination of contaminants from waste water such as Bentonite [9, 10], Chitosan [11], Perlite [12], Kaolin [13], Zeolite [14] and Gypsum [15].

The present work evaluates adsorption potential of alkali feldspar towards Direct Red 16 (synthetic textile dye). Alkali Feldspar (KALSi$_3$O$_8$-NaAlSi$_3$O$_8$) is fundamental ingredient of the earth's crust and is widely used as raw material in glassmaking, ceramic industry and as filler in paints and rubber [16]. Beside industrial uses Alkali feldspar is the essential constituent mineral of granite, granitoids, granodiorite and pegmatite and quartzo-feldspathic veins [17]. In Pakistan, it occurs in intrusive rocks such as Thak Gali complex in Kohistan [18], Malakand granite and granite gneiss [19], Mansehra granite and pegmatites [20] and Neelum and Jura granite in Kashmir [21]. In Mansehra district, the alkali feldspar is economically quarried from acid minor bodies like pegmatites and veins at Atter Sheesha, Batrasi, Chitta Batta and Oghi. Such bodies occur as lenses, veins and swells. In the present study samples of feldspar were quarried from Oghi area (34^0 26′ 15.9″N, 73^0 04′ 51.28″E). Mineralogically these bodies are mainly composed of alkali feldspar, quartz, micas, and tourmalines and garnet at places. Compositionally alkali feldspar exposed in Mansehra area is mainly composed of albeit and microcline with some orthoclase [22].

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Results and Discussion

Adsorption is the process in which molecules of adsorbate are attracted towards the surface of adsorbent. Surface area, temperature, pH, nature of adsorbate, nature of adsorbent and contact time are the prominent factors that affect the whole process of adsorption. Adsorption of Direct Red 16 was studied by optimizing all these parameters.

Effect of Shaking Speed

Effect of shaking speed on the adsorption of DR16 on Feldspar is shown in Fig. 1. Adsorption process was carried out over the range of 50rpm – 300rpm. The optimum shaking speed for removal of DR 16 was found at 200 rpm. Maximum adsorption was 80 percent at 200 rpm and minimum adsorption was 52 percent at 300 rpm. It was observed that in start adsorption yield increases with increasing the speed of shaking and after reaching up to the optimum level there is a sudden decline in percentage adsorption. By increasing the speed further it was observed that system attains equilibrium and no further increase in adsorption takes place. This behavior is shown in Fig. 1. This behavior of adsorption can be explained on the basis of the fact that initially kinetic energy of the particles of adsorbents well as the molecules of dye, increases with the increase of shaking speed. Due to which chances of adsorbent particles to interact with molecules of dye increases and as the result percentage adsorption increases. But after reaching to optimum speed shaking adsorption values dramatically drops. This is understandable because kinetic energy of both adsorbent and adsorbate particles increases so much that collisions starts, due to which weakly bounded molecules of dye become detached from adsorbent particles [23, 24]**.** So for further experiments 200rpm shaking speed was selected.
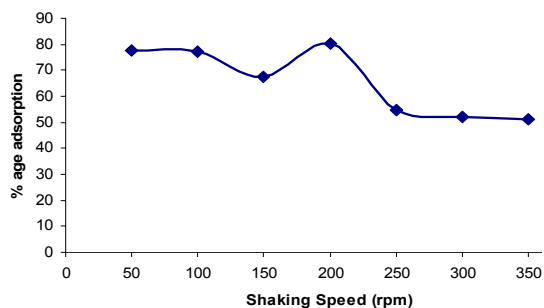

Fig. 1: Effect of Shaking Speed on Adsorption of DR 16 (Contact time; 30minutes, Concentration of analyte; 30ppm, Adsorbent dosage 5g per 50ml and pH 7).

Effect of Adsorbent Dosage

The effect of change in dose of adsorbent on the adsorption process of Direct Red 16 was carried out by using optimum shaking speed 200 rpm. 1g to 8g per 50 ml dose of adsorbent was taken for this experiment. It was observed that initially the adsorption increases as the adsorbent dose increases. After attaining the optimal mass value there was no significant increase in adsorption value as shown in Fig. 2. The minimum adsorption was observed at 42 percent for 1.0 g and maximum adsorption was 83 percent at 7g and 8g. After reaching the maximum adsorption value there was no more significance change in the removal efficiency of DR 16. This indicates that adsorption efficiency is directly associated to the dose of adsorbent. For further experiments 7g/50ml of DR 16 at 200 rpm was used.
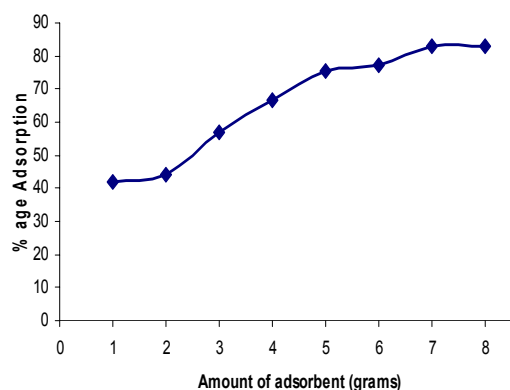

Fig. 2: Effect of adsorbent dose on the adsorption of DR 16 (Shaking speed; 200rpm, Contact time; 30minutes, Concentration of analyte; 30ppm, and pH 7).

Effect of Contact Time

The effect of contact time of both phases was studied to get the optimal contact time between two phases for maximum adsorption. For that adsorption behavior studied from 0-90 minutes with interval of 15 minutes. It was observed that adsorption rate first increases with the increase in contact time. But after attaining the optimum time value, percentage adsorption adsorption decreases and attains equilibrium (Fig. 3). The least value of adsorption was observed at 90min i.e. 60 percent and highest value is 93 percent at 15 minutes. For further experiments 15 minutes contact time was used.
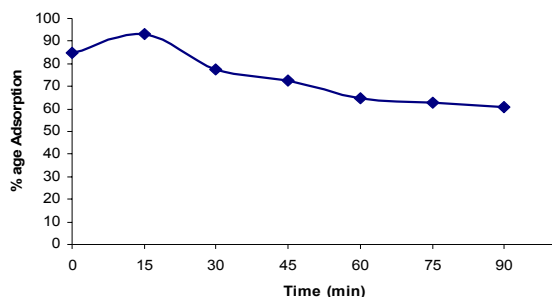
Fig. 3: Effect of Contact Time on the adsorption of DR 16 (Shaking speed; 200rpm, adsorbent dose 7g per 50ml, Concentration of analyte; 30ppm, and pH 7).

This may be justified that in start maximum binding sites are available and molecules of dye become easily attached on these available sites. But after reaching at optimum time value all the available active sites become saturated with dye molecule so a continuous process of adsorption and desorption starts and due to system attains equilibrium. This type of adsorption pattern by using different adsorbents has also been observed by different researchers **[**25, 26**].** In this experiment 15 minutes time was enough for the molecules of dye to saturate all the available binding sites and to fill available surface area at given operational conditions.

Effect of pH

Adsorption process is strongly related with pH of solution. The effect of pH on adsorption of DR 16 was studied. The effect of pH was studied by varying the pH from 2-12 with interval of 2. pH was attained by using 0.1 M HCl and 0.1 M NaOH solutions pH. It was observed that it beginning, by increasing the pH value adsorption efficiency increases but after attaining the optimal pH percentage adsorption value decreases with increase in pH value (Fig. 4).
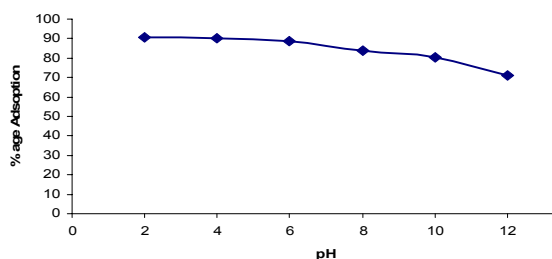

Fig. 4: Effect of pH on adsorption of DR 16 (Shaking speed; 200rpm, adsorbent dose 7g per 50ml, Contact time; 15 minutes and Concentration of analyte; 30ppm).

The adsorption process is critically related with pH factor and variation in pH value affects considerably the adsorption process. It is a known fact that functional groups dissociate from the surface of adsorbent at different pH values. Influence of pH on adsorption also dependent on the chemical composition of solution as well as the functional groups present on the surface of adsorbent. Hydrogen and hydroxyl ion surrounds the surface of adsorbent at highly acidic and basic pH values. So these positive or negatively charged ions start competing with dye molecule as the result of which adsorption of dye molecules decreases [27].

In this particular case DR16 shows maximum adsorption in acidic medium at pH 4.

Adsorption Isotherms

Different adsorption parameters were calculated by adsorption Isotherms. The data obtained from the Batch study was applied on adsorption models including Langmuir and Fruendlich models.

Langmuir Isotherm

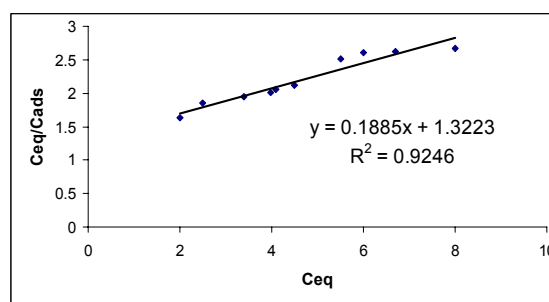Adsorption data of DR 16 on feldspar was subjected on Langmuir Isotherm, Shown in Fig. 5.

Fig. 5: Langmuir adsorption isotherm for DR 16 on Feldspar.

Langmuir Isotherm Equation

$$C_{eq} / C_{ads} = 1 /Qb + C_{eq} / Q \qquad (1)$$

where:

C_{eq} = Equilibrium Concentration of adsorbate
C_{ads} = Adsorbed amount.
Q   = Adsorption capacity.
b   = Energy related Langmuir constant.

C_{eq}/C_{ads} values were plotted against C_{eq}. Straight plot is obtained. The langmuir Parameter Q and b were calculated by using parameters like slopes and intercepts of the linear plots. The Q value was 5.30 mg/g for Direct Red 16.and value of b for Direct Red16 was 0.142 L/ g.

Fruendlich Isotherm

Adsorption data was also applied on Fruendlich isotherm model. Fruendlich Isotherm Equation

$$\log C_{ads} = 1/n \ \log C_{eq} + \log K \qquad (2)$$

where:

1/n = Fruendlich energy constant
K = Max adsorption capacity
$\log C_{ads}$ was plotted against $\log C_{eq}$.

Fig. 6 shows Fruendlich adsorption isotherm of DR 16 on feldspar. The values of K and n were calculated from slope and intercept of the plots. The calculated value of K is 1.251 and value of n is 0.62 for Direct Red 16. The n values indicate the steepness or flatness of slopes. Value of 1/n near to 1 express the steep slope and high adsorption capacity at equilibrium concentrations. While 1/n << 1 indicates flat slope which express the reduced adsorption capacity at low equilibrium condition.
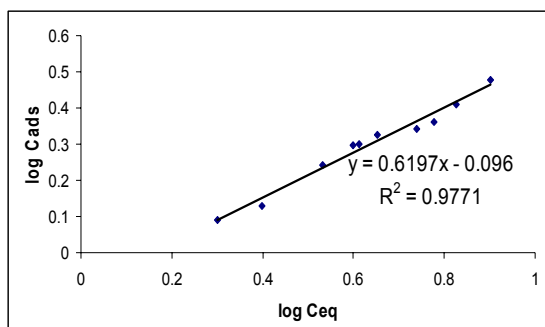

Fig. 6:   Fruendlich adsorption isotherm for DR 16 on Feldspar.

Adsorption Thermodynamics

For thermodynamic study, the adsorption of DR 16 on the feldspar was studied at four different values of temperatures. The range of temperature for this study of adsorption thermodynamics was 293K to 313K. All the optimal conditions that were studied during adsorption parameters were used in this thermodynamics study.

The change in enthalpy (ΔH) was determined from slope and intercept was used for the calculation of entropy (ΔS), of the plot of Log Q against 1/T in Kelvin shown in Fig. 7. ΔG (change in Gibbs free energy) is an important thermodynamic parameter and its value is calculated at four different temperatures by using the equation below.

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

where:

ΔH = Enthalpy change
ΔS = Entropy change
ΔG = change in Gibbs Free Energy
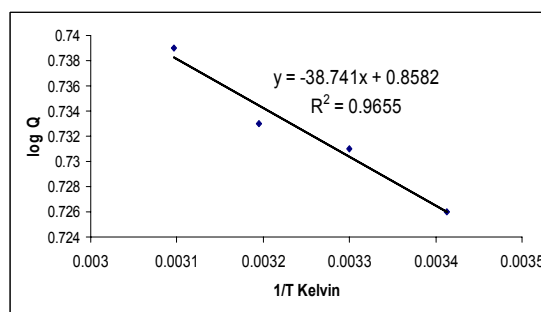T = Temperature in Kelvin

Fig. 7:   Plot of Langmuir isotherm constant (InQ) of DR16 vs Temperature (1/T).

The positive values of ΔH indicate that process of adsorption is of endothermic nature while negative values of ΔG indicate the spontaneous nature of adsorption process. The calculated values of ΔG, ΔH and ΔS are shown in Table-1.

Table-1: Thermodynamic Constants for the adsorption of DR 16 on feldspar at various temperatures.

Temp (K)	ΔG (KJ mol⁻¹)	ΔH (KJ mol⁻¹)	ΔS (KJ mol⁻¹ K⁻¹)	R (KJ mol⁻¹ K⁻¹)
293	-1.7593			
303	-1.8303	0.321	0.0071	(0.0083)
313	-1.9013			
323	-1.9723			

FTIR Characterization

FTIR of feldspar before and after treatment with direct red 16 were taken i.e. Fig. 8 and 9. For that the first step was the identification and confirmation of presence of functional groups, which can act as possible active sites for the dye molecules. As shown in Fig. 8, in untreated feldspar peaks were observed at 3628, 1872, 1795, 1687, 1598, 1433, 1010, 788 and 698 cm⁻¹. There is a slight shift in some frequency bands or peaks in dye loaded feldspar after adsorption which shows the attachment of dye molecules on the functional groups present on adsorbent.
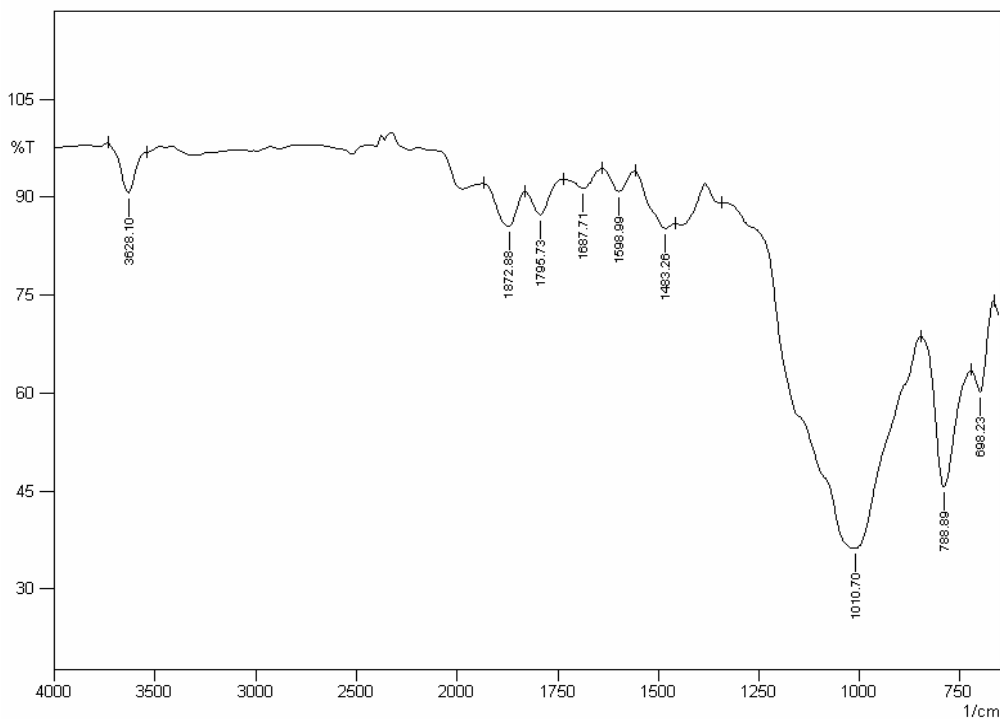
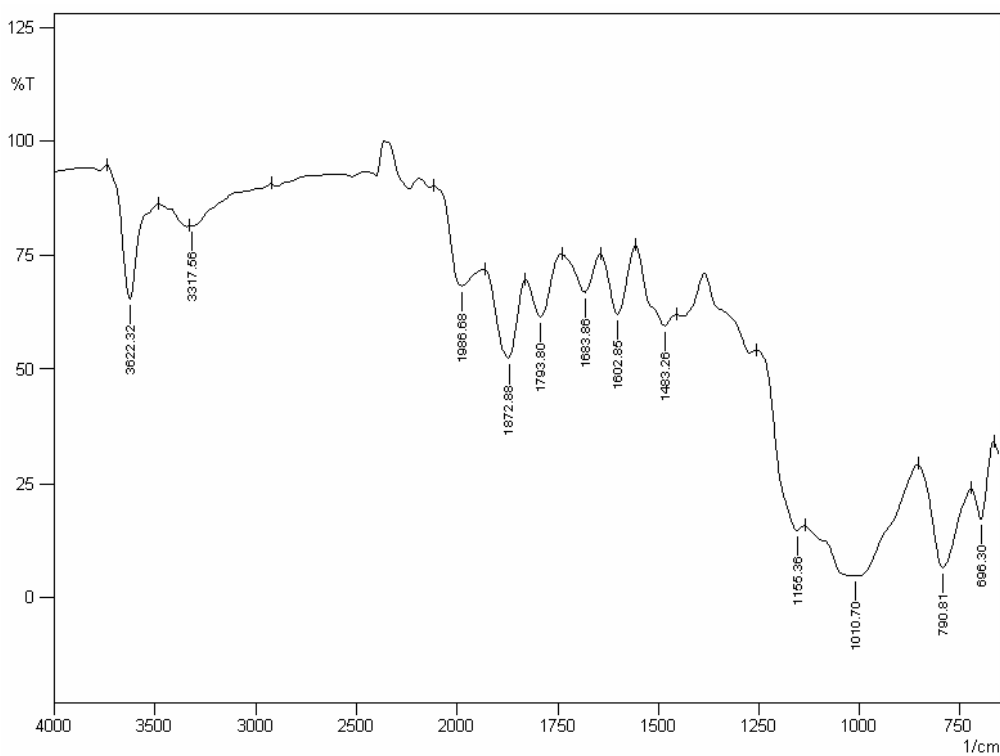Fig. 8:   FTIR analysis of feldspar without treatment.

Fig. 9:   FTIR analysis of feldspar after treating with DR16.

Experimental

Chemicals, Reagents and Equipment

All chemicals, reagents and equipment used during this study were of analytical grade. Deionized water was used for the preparation of solution and dilution of solutions when required. Glass ware was thoroughly washed with chromic acid, Tap water and finally with distilled water. pH values of the solutions were adjusted by 0.1 M solution of NaOH and HCl using pH meter (Lovibond pH 200).For Batch set up conical flasks of 250ml along with orbital shaker (SHO-2D WiseMix, Daihan Scientific) were used. The concentrations of Direct Red 16 solutions (standard as well as sample) were measured with the help of UV/VIS spectrophotometer (Lovibond, Spectro UV-Vis double beam 3500) at λmax = 528 nm.

Adsorbent Preparation

Sample of feldspar was collected from Oghi, Mansehra District, Pakistan. This sample was then washed thoroughly to remove dust and dirt, and dried. It was then grinded and sieved in a mechanical sieve shaker to get the pass of sieve No. 80 and retain of sieve No. 100. This pass was then dried in oven and saved in desiccators for further use.

Stock Solution and Standards Preparation

Stock solution of 1000ppm concentration of DR16 was prepared by dissolving 1000mg/L of DR16 (Merck) in doubly distilled water. Further dilutions were made by appropriate dilutions of the stock solution.

Batch Study

To find out optimum conditions batch set up of experiments were performed. For this set up 250ml conical flasks were used on the platform of orbital shaker. 50ml solution of DR 16 having concentration 30ppm was used in every experiment to evaluate optimum value of parameter under study. To study the effect of shaking speed over the range of 50-300rpm, 5g per liter adsorbent dose was used at room temperature, pH was adjusted to 7 and contact time of two phases was 30 minutes. After that the solution was filtered to separate adsorbent and filtrate. UV/Vis spectrophotometer was used to find out the remaining concentration of DR16 in solution. Similarly in the next experiment most effective shaking speed was used as optimum speed, while adsorbent dose varied from 1-8 g/50ml of the

solution, at room temperature, pH was adjusted to 7 and contact time of both phases was 30 minutes. Afterwards the same procedure of filtration and determination of remaining concentration was followed as described earlier. Studying the effects of contact time and pH, same experiments were repeated at room temperature in accordance with the results of earlier findings. In order to ensure accuracy every experiment was replicated thrice and mean values of the results were employed for calculations.

Conclusions

The adsorption behavior of Direct Red 16 (textile Dye) on naturally occurring and cheap geological material Feldspar has been studied in detail. It was found that maximum adsorption has taken at 200 rpm shaking speed, 7g per 50ml adsorbent dose pH4 and 15 minutes contact time of both phases. Two adsorption models Langmuir and Fruendlich were subjected to explain the adsorption phenomenon. Maximum adsorption capacity of DR16 was 5.3mg per gram of feldspar. Thermodynamic study showed that this adsorption system is spontaneous and favorable. So it was concluded that Feldspar can be effective and excellent adsorbent for removing hazardous DR16 from textile effluents.

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