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Alumina as environmentally stable adsorbent for the removal of diresul black dye from waste water

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Abstract

Various adsorbents for the removal of dyes from waste water may or may not be stable, resulting in the desorption of adsorbed dyes with slight changes in physical conditions. To avoid this problem, environmentally stable adsorbent such as activated aluminum oxide or alumina has been used for the removal of Diresul Black, which is a dye used in the textile processing industry. Fourier-transform infrared spectroscopy confirms the non-tetrahedral framework of alumina. The efficiency of alumina via adsorption implies that 1 g alumina having the Brunauer–Emmett–Telle surface area of 2.65 $\pm$ 0.25 m^2/g is enough to achieve up to 85% removal of concentrated dye solution in just 20 minutes. Adsorption energy as well as adsorption capacity is calculated by different adsorption isotherms. The sorption energy E turns out to be 19.3 KJ/mol. The thermodynamic studies show that the value of ΔH for the adsorption process is $-$976.5 J/mol while that of ΔS is $-$4.748 J/mol/K. Desorption studies show that the dye remains in its adsorbed form over aluminum oxide up to a pH of 2. Various ions present in the matrix interfere with the adsorption process, however none can decrease the adsorption below 65%.

Key words: adsorption, alumina, desorption, diresul black, thermodynamics

INTRODUCTION

Large molecular structures of dyes with aromatic properties make them more resistant and less biodegradable. Moreover, dyes are poisonous for several species of microbes and cause direct inhibition and disruption of their catalytic activities (Dash 2010). If dyes are not treated properly in waste water, they have the tendency to cause considerable environmental degradation (Malik 2002). Dyes have a propensity to sequester metal ions, resulting in micro toxicity to fish and other organisms (Dash 2010).

Sulfur dyes, of which sulfur black (Diresul Black) is one type, are two-part dyes mainly used for dyeing and printing of cellulose fiber and/or cellulosic blended textile fibers. They are preferred by textile manufacturers for the deep colours and darker shades they produce on the final fabric. Although the Diresul dyes are considered to be less harmful ecologically, in developing countries, however, due to the lack of processing of the effluents, many environmentally harmless substances may cross the threshold after which they start to conflict with the environment. Adsorption is an important process: better in various ways than other processes of removal of undesired substances like chemical precipitation, extraction, coagulation and colour discharge, etc. (Che Ani 2004).

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Aluminum oxide or alumina (Al_2O_3) is activated from aluminum hydroxide by dehydroxylating it in dry oven at 105 °C that produces a highly porous material. Owing to the presence of Lewis acid sites, alumina has the capability to withdraw electrons, making the adsorption rate faster (Kannan *et al.* 2008). Due to this property of Alumina and the reason that it has already been used and proven to be environmentally stable by Kannan *et al.*, our present work focuses on its utilization to remove Diresul Black dye.

In the present work, not only is the adsorption of Diresul Black studied, but also the impact of various ions, which may be useful or toxic, that are present in the waste water streams on the process of adsorption. This is because the following procedure will ultimately be extended to large scale cleaning of waste water containing the dye (Ahmad *et al.* 2006).

Desorption of the dye in various acidic media and their concentrations is studied because usually the adsorption phenomenon is limited due to the presence of acids in the aqueous media. Since this work needs to be extended to the real waste water streams, the desorption phenomenon was also studied.

Our hypothesis states that Alumina when activated yields a non-tetrahedral framework, which is an environmentally stable adsorbent and so it will adsorb Diresul black dye spontaneously through chemical adsorption, even in the presence and influence of other ions commonly present in the real water streams and it will not desorb to a greater extent even with the changes in physical conditions such as pH, accomplished by using various acids in different concentrations.

METHODOLOGY

Analytical grade chemical compounds mostly acquired from Sigma-Aldrich and Merck have been utilized for the present work. Diresul Black dye, oxalic acid, citric acid, perchloric acid, nitric acid, hydrochloric acid and aluminum oxide were the main chemicals used in this study.

The overall methodology includes a systematic study starting from the activation and characterisation of Alumina in order to confirm that a non-tetrahedral structure of the adsorbent has been achieved with the generation of Lewis acid sites (Kannan *et al.* 2008). The adsorption process has been optimised to determine the optimum contact time, temperature, concentration and weight of the adsorbent for achieving maximum percentage of adsorption. The concentration optimisation is also used to find out parameters which would be used to evaluate various isotherms.

Activation and characterisation of adsorbent

Before the adsorption experiment, alumina (Merck) was activated at 150 °C for 3 h in a hot-air oven (Model no: M0144OC-1). The Fourier-transform infrared spectroscopy (FTIR) spectrum of alumina was recorded in the range of 4,000–500 cm^{-1}.

Adsorption experiments

1 g of activated alumina was added in 10 mL of dye for adsorption. The mixture was shaken at 150 rpm on shaker (HeidolphUnimax 1010). Spectrophotometry was employed to measure the final concentrations at 650 nm. Percentage sorption was calculated from the equation:

$$\%age\ sorption = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Here C_o is the initial concentration of the dye before adsorption and C_e is the equilibrium concentration, i.e. the concentration of dye after equilibration with the aqueous solution.

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and the R_d value was calculated as:

$$R_d = \frac{amount\ of\ dye\ on\ adsorbent}{amount\ of\ dye\ insolution} \times \frac{volume\ of\ solution\ (V)}{weight\ of\ dry\ adsorbent\ (w)} cm^3/g \quad (2)$$

R_d refers to the distribution coefficient, i.e the ratio of solute (in this case the dye) adsorbed on the adsorbent to that in unabsorbed form within the aqueous solution.

In order to optimize the adsorption process, various parameters were taken into account and are given in the results section (Ahmad *et al.* 2006).

Desorption experiments

Oxalic, citric, perchloric, nitric and hydrochloric acids were used to make the media acidic so that our hypothesis could be tested, which stated that Alumina is environmentally stable and would not deteriorate under changing physical conditions such as pH. A combination of a few of the above acids was used to find whether the desorption was achieved faster. At 29 °C, an adsorbent amount of 1 g and contact time of 20 min, which are the optimized conditions for maximum adsorption, the desorption experiments were carried out by shaking the adsorbed alumina within the aqueous solution and keeping this contact for 24 hours, adding different acids and acid combinations one by one.

RESULTS

FTIR spectrum of alumina

Figure 1 shows the FTIR spectrum of alumina. The band observed at 1,605 cm^{-1} might be the asymmetric stretching (Al–O–Al) and similarly, symmetric stretching is observed at 606 cm^{-1} by using FTIR spectrophotometer (Midac Corporation Irvine, California, US, M2000). The broad peak at 3,455 cm^{-1} is due to uncondensed –OH groups.

Adsorption studies

Effect of contact time

The adsorption contact time was studied on alumina in a 0.0124 M dye solution (Figure 2). The other adsorption parameters like temperature and adsorbent concentration were constant. As shaking time

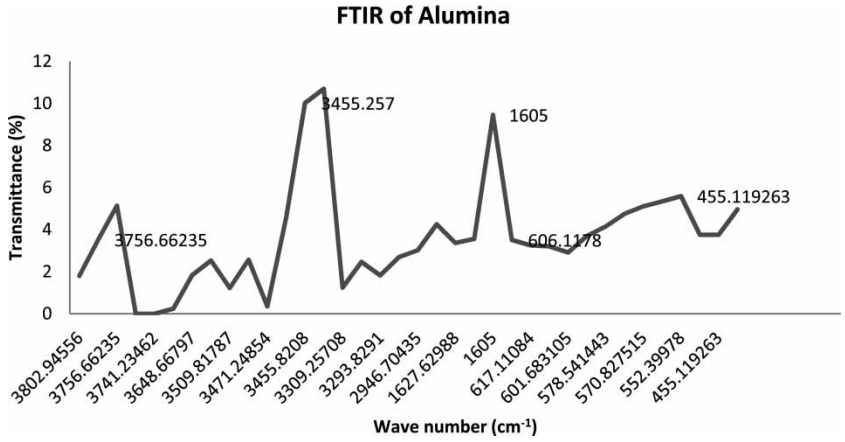

Figure 1 | FTIR spectrum of alumina.

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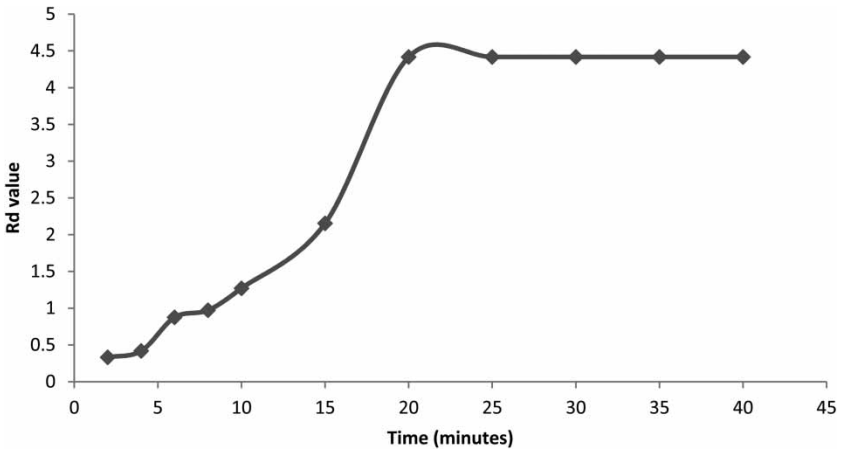

Figure 2 | Effect of contact time on R_d value for Diresul Black's adsorption on alumina: temperature = 29 °C; dye concentration = 0.0124 M; adsorbent amount = 1 g.

increased, the value of distribution coefficient also increased; at 20 min shaking of sample, increasing the shaking time caused no change in adsorption of Diresul black on alumina. Hence, the equilibration time is recognised as 20 minutes. Figure 2 indicates that by increasing the shaking time from 2 minutes to 10 minutes, the R_d values increase. This result shows that in the real water streams, under varying conditions of temperature and acid content, this contact time may change further but would still not be too long and therefore feasible.

Effect of concentration of dye:

Keeping all the other parameters constant, changing the concentration of Diresul Black had a profound impact on the adsorption percentage. It was found to increase the higher the Diresul Black concentration, but after 0.0124 M, adsorption decreased as concentration of dye increased, mainly because of the saturation of active sites. Hence there is a marked decrease in the distribution coefficient values with increase of dye concentration (Figure 3). The percentage sorption and R_d values are closely related however percentage sorption actually implies the amount that has gone into the adsorbent while the R_d value shows the distribution between the adsorbate, the solution and the adsorbent.

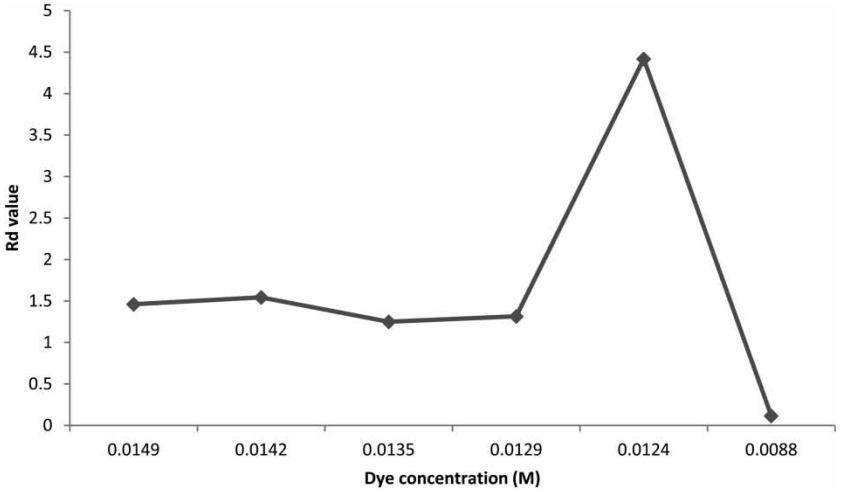

Figure 3 | Effect of dye concentration on R_d value for adsorption of Diresul Black on alumina: temperature = 29 °C; adsorbent amount = 1 g; contact time = 20 min.

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Impact of adsorbent dose

Increasing the adsorbent dosage from 0.70–1.20 g increased the percentage removal and the distribution coefficient value of the dye. The equilibration was attained at 1 g of alumina addition, as a result adding more adsorbent had no effect on dye adsorption (Figure 4). This is because the corresponding concentration of adsorbate is not changing and the saturation of active sites is reached.

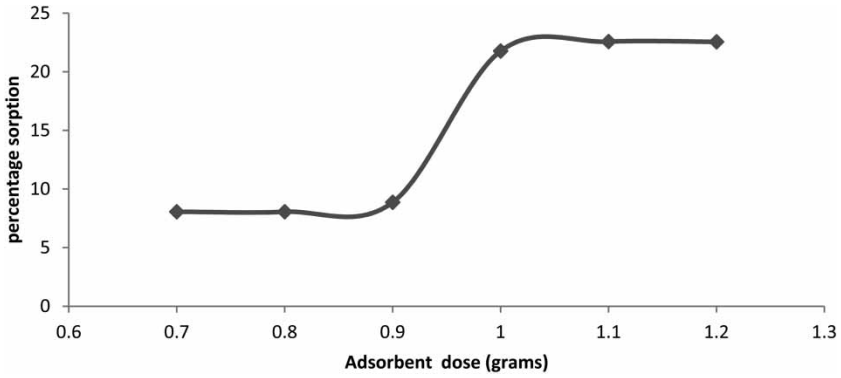

Figure 4 | Effect of adsorbent amount on percentage sorption of Diresul Black on alumina: temperature 29 °C; dye concentration 0.0124 M; contact time 20 min.

Effect of temperature

Temperature can significantly influence the adsorption process. Adsorption increases with temperature as more sites are activated on the surface of alumina for more dye adsorption or enhance diffusion of sorbate species. By calculating the fraction of sorption we can find value of K_c which is the equilibrium constant given in Equation (3) (Achmad *et al.* 2012). Equilibrium constant is merely a ratio of fraction of dye that is adsorbed to the fraction which remains unadsorbed in the solution. A straight line is obtained by plotting log K_c vs. 1/T (Figure 5).

$$K_c = \frac{f}{1-f} \tag{3}$$

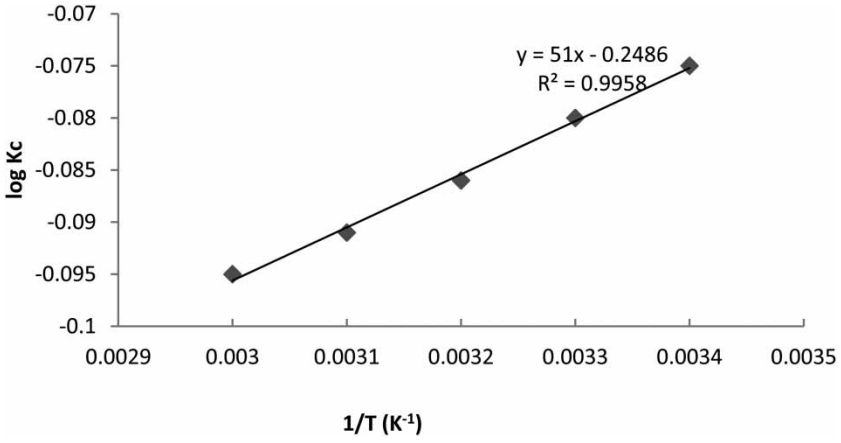

Figure 5 | Graph of log K_c vs. 1/T showing effect of temperature change on Diresul Black's adsorption on alumina: adsorbent concentration 1 g; dye concentration 0.0124 M; contact time 20 min.

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with f representing fraction of adsorbed dye. Following relations are used for the determination of thermodynamic parameters:

$$\Delta G = -RTlnK_c \tag{4}$$

$$\log K_c = -\Delta H/2.303RT + \Delta S/2.303R \tag{5}$$

where ΔG, ΔH and ΔS are the Gibbs free energy, enthalpy and entropy changes of adsorption process. The value of ΔH comes out to be -976.5 J mol^{-1} while that of ΔS is calculated as -4.748 J mol^{-1} K^{-1}. These values indicate the negative values of Δ G referring to the spontaneous nature of the sorption of Diresul Black onto aluminum oxide. Actually, higher temperature creates more active sites on the surface of aluminum oxide and helps in the enhancement of diffusion of the adsorbate molecules.

Adsorption isotherms

Various isotherms have been studied in order to find out the nature of adsorption. Langmuir isotherm was applied to see whether there is an indication of monolayer formation in the process. The isotherm in its linear form is represented as (Langmuir 1918):

$$C_e/C_{ads} = 1/Mb + C_e/M \tag{6}$$

where C_{ads} is the amount of dye adsorbed from the medium and C_e is its equilibrium concentration, M represents the maximum amount of solute adsorbed and b is a constant related to the binding energy of solute. The sorption data does not fit well with the Langmuir isotherm, not yielding a straight line when the equation was plotted, which is a general criteria to confirm the validity of monolayer formation based on the surface homogeneity (Shang *et al.* 2005). This implies that simple condensation is not taking place in this case of sorption. Rather, active sites are somehow involved.

Freundlich isotherm was applied to see surface heterogeneity through the evaluation of the intensity of adsorption and maximum sorption capacity. A linear form of Freundlich isotherm is given below (Freundlich 1962):

$$log\, C_{ads} = log\, C_m + 1/n\ log\, C_e \tag{7}$$

C_m is the maximum sorption capacity and 1/n refers to the number of active sites. Plot between $log\ C_{ads}$ *vs.* $log\ C_e$ gives the value of n equals to 7.6 ($n > 1$), which shows a greater intensity of adsorption while the maximum sorption capacity is 7.244 mmoles/g (Figure 6). The value of 1/n indicates the relative distribution of energy sites and depends upon the nature and strength of the adsorption process. According to the linearly transformed equations and least-squares methods, the sorption data has been translated such that 1/n turns out to be a heterogeneity parameter; a smaller 1/n shows greater expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/n = 1$. If n lies between one and 10, this indicates a favourable sorption process.

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. It is used to calculate the sorption energy which indirectly draws a boundary between the chemical or physical adsorption (Dubinin & Radushkevich 1947).

$$lnC_{ads} = ln\, X\, m - \beta\varepsilon 2 \tag{8}$$

Maximum sorption capacity is given by Xm, ε is the polannyi potential and β (kJ^2 mol^{-2}) which is an essential constant for calculating the sorption energy.

$$\varepsilon^2 = RT \ln\left(1 + \frac{1}{C_{eq}}\right) \tag{9}$$

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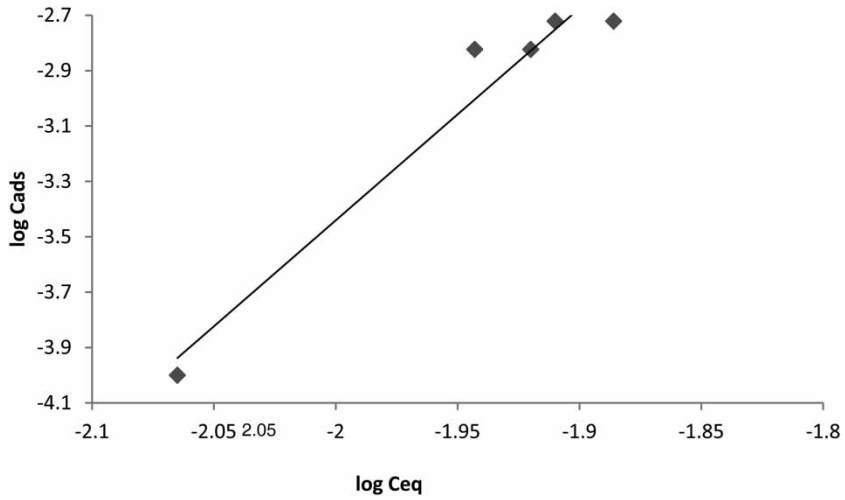

Figure 6 | Freundlich adsorption isotherm for the sorption of Diresul Black on alumina.

The Polannyi adsorption potential refers to the assumption of this theory stating that molecules near the surface move according to the potential similar to that of electric field or gravity. Plot between ln C_{ads} and give the value of β as -13.40×10^{-4} kJ^2 mol^{-2} (Figure 7), from this value, the sorption energy was determined by using formula:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{10}$$

Calculated value of E is 19.3 KJ/mole that shows Diresul Black adsorbs on alumina via chemisorption, X_m the maximum sorption capacity is calculated to be 2.410 mol g^{-1}. According to the approach, mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity) less than 8 KJ mol^{-1} depicts physical adsorption, while more than this value shows chemisorption (Ahmad *et al.* 2006).

As a general review to all the isotherms, the value for regression analysis for both Freundlich and D-R isotherm is close to unity, i.e. 0.949 and 0.955 respectively. The values for maximum sorption capacity as calculated by both Freundlich and D-R isotherm differ, but they have the same order of magnitude. The difference, which is observed in the values for the same parameter, can be due to

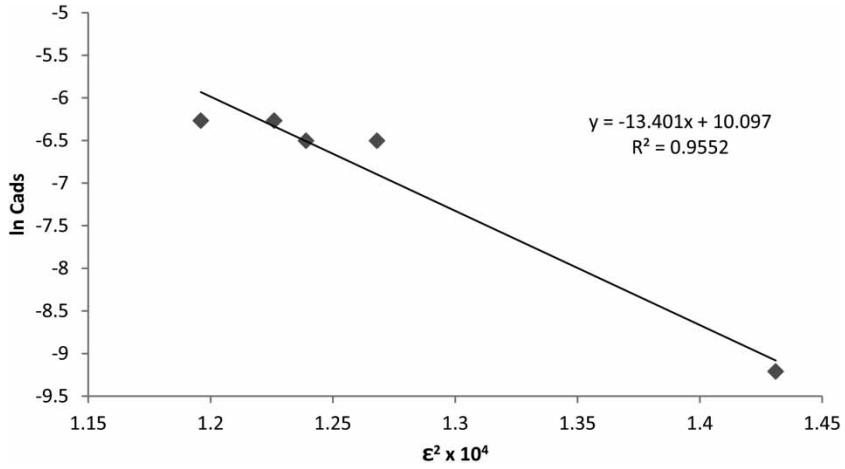

Figure 7 | Dubinin-Radushkevich isotherm for the sorption of Diresul Black on alumina.

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the fact that these isotherms were originally derived for the adsorption of gases on different sorbents, so they cannot be generalized on every system although they usually fit the adsorption data very well.

EFFECT OF ADDED IONS ON THE ADSORPTION

Some ions like potassium, sulphide, chromium and lead tend to enhance the adsorption, while others suppress it as seen from Table 1. Sodium, copper, magnesium, iodide, sulphate and carbonate do not have much influence on this adsorption and therefore the distribution coefficient value remains the same, even after the addition of these ions.

The impact of various ions on the adsorption process and the enhancement or suppression of the percent sorption values can be attributed to the fact that there may be the formation of complexes of few ions with Diresul black having increased affinity for adsorption, thereby increasing the percent sorption values, or this increase might have happened due to the creation of additional adsorption sites. The reduction in sorption due to the presence of ions may be due to their stronger affinity for sorption, thereby decreasing the chances of sorption for Diresul black by decrease in sorption sites.

DESORPTION STUDIES

Figure 8 depicts the percentage of desorption clearly indicating that weak acids like citric and oxalic acid do not contribute much to desorption and even after 24 hours' contact they cannot desorb the dye to an appreciable extent. The acids like HNO_3 and HCl at their higher concentrations can desorb the dye, while $HClO_4$ requires a very high concentration to start the desorption process,

Table 1 | Impact of various ions present in the adsorptive medium on the sorption of diresul black onto alumina. The optimized conditions are temperature = 29 °C; adsorbent amount = 1 g; contact time = 20 min., dye concentration = 0.0124 M

Added Ion under Consideration	$R_d(cm^3 \cdot g^{-1})$
None (optimum condition)	$4.3 \times 10^3 \pm 2.2$
Zinc (Zn^{2+})	$3.8 \times 10^3 \pm 3.2$
Potassium (K^+)	$5.8 \times 10^3 \pm 4.6$
Sodium (Na^+)	$4.2 \times 10^3 \pm 3.5$
Copper (Cu^{2+})	$4.1 \times 10^3 \pm 3.2$
Magnesium (Mg^{2+})	$4.2 \times 10^3 \pm 3.2$
Calcium (Ca^{2+})	$3.9 \times 10^3 \pm 2.2$
Sulphide (S^{2-})	$4.8 \times 10^3 \pm 3.2$
Oxalate ($C_2O_4^{2-}$)	$2.3 \times 10^3 \pm 1.2$
Selenium (Se^{4+})	$3.3 \times 10^3 \pm 2.4$
Nitrate (NO_3^-)	$2.8 \times 10^3 \pm 2.5$
Bicarbonate (HCO_3^-)	$3.6 \times 10^3 \pm 2.2$
Chloride (Cl^-)	$3.3 \times 10^3 \pm 2.1$
Bromide (Br^-)	$2.3 \times 10^3 \pm 1.2$
Iodide (I^-)	$4.2 \times 10^3 \pm 3.2$
Carbonate (CO_3^{2-})	$4.3 \times 10^3 \pm 3.1$
Sulphate (SO_4^{2-})	$4.2 \times 10^3 \pm 2.2$
Chromium (Cr^{3+})	$6.3 \times 10^3 \pm 4.2$
Lead (Pb^{2+})	$5.3 \times 10^3 \pm 4.1$

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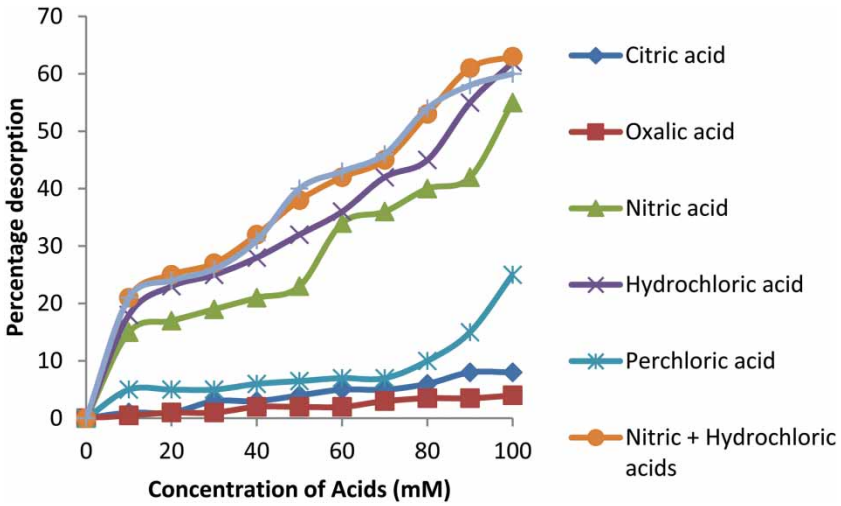

Figure 8 | The desorption percentage of Diresul black from alumina by addition of different concentrations of various acids and acid combinations.

giving a smaller percentage of desorption. A combination of acids is however effectively desorbing the dye from Alumina.

CONCLUSION

At the beginning of study, we hypothesized that the non- tetrahedral alumina is environmentally stable due to the occurrence of Lewis acid sites, and there will be chemisorption between Diresul Black and non-tetrahedral alumina. This hypothesis turned out to be a reality. Under acidic environments and high temperatures, the desorption percentage remains low (with an exception of combination of few acids) indicating that merely by changing the physical parameters, the desorption within the waste water streams will not occur. Impact of various usually present ions show that there are few ions which can effectively hinder the process of adsorption.

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