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Synthesis and adsorption efficiency of calix[6]arene appended XAD-4 resin

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ABSTRACT

This study describes the synthesis of calix[6]arene hexaester appended Amberlite XAD-4 (resin 2) and its application for the removal of reactive blue-5 (RB-5) and direct black-38 (DB-38) azo dyes from aqueous media. The newly synthesized resin 2 was characterized by using various analytical techniques such as FTIR spectroscopy, elemental analysis, scanning electron microscope, and thermogravimetric analysis. In this approach, adsorption efficiency of resin 2 for azo dyes was explored by optimizing various parameters such as pH, adsorbent dose, role of electrolytes, and contact time. From results it has been observed that percentage adsorption of these azo dyes is highly dependent on pH of the solution. The maximum adsorption of RB-5 and DB-38 was achieved at pH 3 and pH 9, respectively. Isotherm evaluation has judged that adsorption behavior can be better demonstrated by Langmuir and D–R models. The kinetic studies revealed that removal process of selected dyes follow pseudo-second-order kinetic model. The positive and negative values of ΔH and ΔG, respectively, confirm the endothermic and spontaneous nature of this adsorption process. Moreover, results shows that resin 2 has proved highly effective adsorbent for the removal of azo dyes from aqueous environment.

Keywords: Calix[6]arene; Amberlite XAD-4; Adsorption; Dyes; Isotherms; Kinetic

1. Introduction

Since inception of this universe, humans have been employing different natural sources of colorants for dyeing or painting of their clothes, homes, surroundings etc. From inspiration of their increasing demand and usage a new horizon of synthetic dyes originated after mid of the nineteenth century. According to recent reports, approximately more than 10,000 different dyes and pigments have been synthesized across the world so far with a total annual production over 7×10^5 metric tons per year [1,2]. Industrial globalization of dye stuffs has led to great enhancement in their utilization. According to some estimation, about 280,000 tons of textile dyes are annually liquidated as industrial outflows. Industrial effluent substantially produces non-aesthetic pollution even though these colored substances are present below 1 ppm. As the result of various chemical reactions taking place inside of aqueous environment where they generate eutrophication and dangerous by-products [3,4]. Thus it increases environmental hazards as water pollution [5]. Out of total dye consumption azo dyes contributes 70% which reflects them as the largest and representative class of colorants used in various fields such as textiles, fibers, leather, pharmaceutics, pulp and paper,

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dyeing, paint, laser, liquid crystalline display, inkjet printer, and electro-optical devices. Azo dyes are formed by a coupling reaction of aromatic compounds with an aromatic amines via (–N=N–) linkages [6,7]. Reactive black-5 is a reactive azo dye; however, its extensive applications in textile industry have some drawbacks for human. Its longer exposure causes allergic reactions to respiratory tract and even led to cancer [8].

Direct black-38 (DB-38) belongs to benzidine-based azo dye which is one of the challenging and bio resistant organic toxins [9]. Short term toxicity results in eyes irritation while long term exposure causes liver, intestines, and bladder cancer, and human mutation [10]. Even though azo molecules are biologically inactive, they constitute into corresponding aromatic amines by the action of liver enzymes and intestinal micro flora in human body [11,12]. Moreover, these colored compounds are able to bind DNA molecules, and thus, recognized as the root cause of genotoxicity (mutagenecity), carcinogenicity, and direct intoxication of organisms in water [13,14]. Hence, the European Parliament has banned 22 different azo dyes and their harmful intermediates [15]. Certainly, azo dyes are directly related to the environmental pollution, and therefore, the decolorization and reclamation of waste water is an imperative issue of environmental safety [16].

In this regard, considerable efforts have been experienced to flush out colored toxicants from industrial effluents [17–22]. Great devotion has paid by the number of scientists regarding to wastewater treatment by using different technologies including chemical (oxidative processes, Fenton oxidation, H_2O_2, ozonation, and electrochemical process), biological (decolorization by white-rot fungi and other microbial cultures), and physical (membrane filtration, coagulation/flocculation) [23–26]. Notwithstanding their stumpy removal efficiency along with lofty operational costs as well as disposal problems have constrained them in terms of their applications. However, adsorption has proved an efficient and important method that is very useful for the purification of waste water effluents [27–32]. Therefore, several natural and synthetic adsorbents have been utilized for decontamination of industrial wastewater include charcoals, activated carbons [33], zeolites [34], clays [35], chitin [36], chitosan [37], starch and its derivatives [38], peat [39], wheat straw [40], peanut husk [41], lignocellulosic waste [42], bagasse [43], agriculture waste [44], waste orange peel [45], and polymeric resins [46]. By virtue of relatively low adsorption efficiency along with regeneration problems have limited their use in the field of separation science [47–49]. Therefore, investigations are still underway for the development of some innovative, regenerable, and highly efficient adsorbents. Hence, the main goal of this work is to find out an alternate adsorbent with distinct benefits with respect to higher selectivity and enhanced dyes removal capacity. Adsorption by regenerable resins is comparatively more economical and environment friendly [26,50].

As far as the recognition and remediation of harmful and toxic species are concerned, promising synthetic materials such as "*Calixarenes*" with multivariate functionalies and its immobilization onto polymeric surface have enriched separation science with new enthusiasm [51–54]. In continuation of our previous studies on selected azo dyes remediation, [47,48,50,55,56] herein, we report the synthesis and adsorption study of calix[6]arene based hexaester appended Amberlite XAD-4 resin (resin 2). The main focus of this study is to enhance the adsorption efficiency of Amberlite XAD-4 resin toward selected azo dyes from aqueous environment.

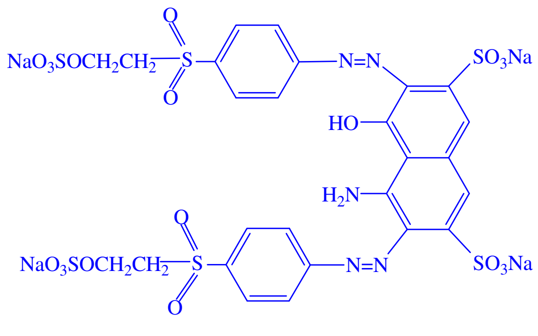
2. Experimental

2.1. Reagents

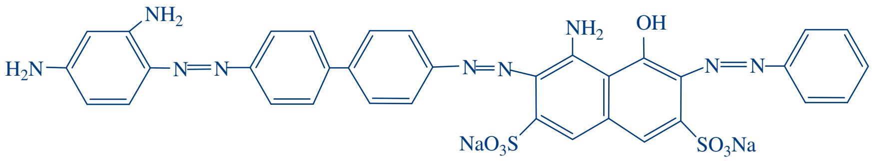
The commercial textile dyes remazol black B/reactive black-5 (991.82 g/mol, $C_{26}H_{21}N_5Na_4O_{19}S_6$) and chlorazol black/DB-38 (781.73 g/mol, $C_{34}H_{25}N_9Na_2O_7S_2$) azo dyes (Fig. 1) was purchased from Sigma-Aldrich (St. Louis, MO, USA) commercially available source and used as adsorbates without any further purification. The wastewater samples were collected from textile and dyes manufacturing industries. The appropriate amount of (0.1 N) HCl/NaOH was used to maintain the desired pH. All chemicals used were of analytical grade. Silica gel (230–400 mesh) was procured from Fluka (Germany). Analytical TLC was performed on precoated silica gel plates (SiO_2, Merck PF_{254}). Deionized water that had been passed through a Milli-Q system (Elga Model Classic UVF, UK) was used for the preparation of solutions.

2.2. Apparatus

Elemental analyses were performed using a CHNS elemental analyzer (model Flash EA 1112, 20090-Rodano, Milan, Italy). Melting points were determined on a Gallenkamp apparatus model (MFB. 595. 010 M England). IR spectra were recorded on a Thermo Nicollet 5700 FTIR spectrometer (WI. 53711, USA) as KBr pellets. Scanning electron microscopic (SEM) studies were performed using JSM-6380 instrument. UV–vis spectra were obtained with Perkin Elmer



Reactive Black-5



Direct Black-38

Fig. 1. Chemical structure of RB-5 and DB-38 azo dyes.

(Shelton, CT06484 USA) Lambda 35 UV–vis spectrophotometer. The pH measurements were made with pH meter (781-pH/Ion meter, Metrohm, Herisau Switzerland) with glass electrode and internal reference electrode. A Gallenkamp thermostat automatic mechanical shaker (model BKS 305-101, UK) was used for batch study.

2.3. Synthesis

The synthesis of compounds I–III were carried out by using previously reported procedures [57–59].

2.3.1. Grafting of hexaester calix[6]arene (III) onto modified Amberlite XAD-4 resin (1)

Synthesis of diazonium derivative of Amberlite XAD-4 (1) was carried out by using previously reported method [60].

The diazotized resin 1 (2 g) was reacted with calix[6]arene (III) (2 mmol, 1.06 g) in 400 mL of glacial acetic acid and acetone (3:1) at 0–3°C for 30 h. The resulting grayish colored beads of resin 2 were filtered off, washed with distilled water as well as chloroform in order to remove the excess or unreacted calix[6]arene (III) and then dried in vacuum oven. 15.5% of calix[6] arene (III) immobilized onto the surface of Amberlite XAD-4™.

2.4. Adsorption procedures

2.4.1. Batch method

For RB-5 and DB-38 azo dyes removal efficiency of resin 2 from aqueous media was carried out by applying batch test methodology. Different parameters such as amount of dosage, pH, contact time, temperature, dye concentration, and effect of electrolytes were also optimized. The experiments were conducted in 25 mL Erlenmeyer flasks with glass cap which contained particular amount of the adsorbents as well as specific concentration of adsorbate. Each test consisted of 10 ml of (2×10^{-5} M) azo dye solution. For equilibrium, the Erlenmeyer flasks containing 10 ml azo dye solution were stirred on a horizontal shaker operating at a constant speed (120 rpm) at 25°C for 1 h. The mixture was filtered off and residual concentration of the organic moiety was determined by means of a UV–vis spectrophotometer. Absorbance values were recorded as λ_{max} for each of the solution at 597 nm for RB-5 and 592 nm for DB-38.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR spectra

Newly synthesized resin 2 was characterized by FTIR spectroscopy. Some important characteristics bands for different functional groups were observed in the spectrum of resin 2. The band observed at 3,451 cm^{-1} was assigned to –OH stretching. While the band observed at 2,916, 1,735, 1,600, 1,437, and 1,368 cm^{-1} are assigned to the asymmetrical stretching for C–H, C=O, N=N, C=C, C–C, and –C–N groups, respectively. Therefore, presence of characteristic vibration bands of newly synthesized resin 2 for C=O, N=N, and –C–N groups can be clearly observed at 1,735, 1,600, 1,437, and 1,368 cm^{-1}, respectively. These diagnostic peaks confirms the immobilization of hexaester derivative of calix[6]arene (III) onto the resin 2.

3.1.2. SEM

Fundamental physical properties and surface morphology of adsorbent surface is generally characterized by SEM. It has been used for determining the particle shape, porosity, and appropriate size of the adsorbent. The morphological characteristics of resin 2 was determined through SEM by applying 05 kV electron acceleration voltage. The spherical shape XAD-4 resin beads were covered by a thin layer of immobilized material, i.e. (III). The presence of attached calix[4]arene moiety as a thin shining layer onto the smooth surface of pure XAD-4 (1) confirm the immobilization.

3.1.3. Thermo gravimetric analysis (TGA)

TGA was used to examine the thermal stability of resin 2. Thermal degradation curve of resin 2 shows two main steps. The first step (ranging from 35 to 130˚C) was assigned to the loss of physically adsorbed water. During this step, only 8% of the total weight was lost. The second step (ranging from 200 to 440˚C) was recognized to the calix[6]arene (III) ring combustion.

3.2. Adsorption studies

3.2.1. Effect of adsorbent dosage

The effect of adsorbent dosages of pure Amberlite XAD-4, hexaester calix[6]arene (III) and resin 2 for the removal of selected azo dyes RB-5 and DB-38 was investigated by varying adsorbents dosage that ranges from 25 to 150 mg and keeping fixed concentration (2×10^{-5} M) 10 ml of azo dyes as shown in (Fig. 2). From experiments, it was deduced that percentage adsorption of azo dyes increased by increasing the resin 2 dosage. It was observed that 88% adsorption of RB-5 dye was achieved only by using 50 mg of the resin 2. There was only a minor increase in percentage adsorption up to 75 mg and it remained almost constant at higher dosages, i.e. 50–150 mg. Similarly, in the case of DB-38, 77% of dye was removed by using just 50 mg of resin 2 and there was no increment in adsorption with the rise of dosage from 50–150 mg. Means at 50 mg, resin 2 surface has been fully saturated with azo dyes and after 50 mg, there was no more adsorbent surface available for azo dyes adsorption. Thus, all the experiments were carried out at a fixed amount of resin 2, i.e. 50 mg.

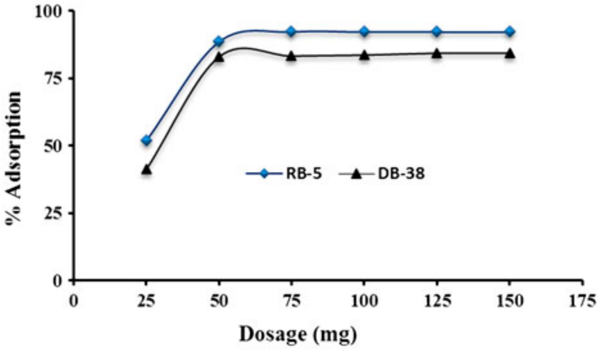


Fig. 2. Effect of adsorbent dosage (25–150 mg) on the percent adsorption of RB-5 and DB-38 azo dyes (60 min of contact time, 0.3 M of NaCl and 10 mL of dye concentration 2×10^{-5} M).

3.2.2. Influence of NaCl concentration on the adsorption of azo dyes

The influence of ionic strength on the adsorption capacity of resin 2 toward selected RB-5 and DB-38 azo dyes was also monitored by varying the molar concentration of NaCl as 0–0.4 mol/L as in (Fig. 3(a)). It was noticed that with the addition of NaCl to dye solution adsorption capacity of resin 2 increased greatly. This is due to the fact that NaCl provides an ionic balance between the solid and liquid phases. Beside this, NaCl increases the solubility of azo dyes

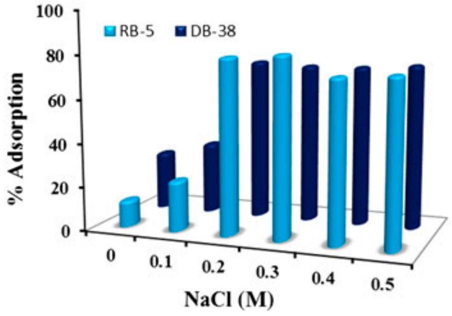


Fig. 3(a). Effect of NaCl concentration on RB-5 and DB-38 azo dyes adsorption (50 mg of resin 2, 1 h of contact time and 10 mL of dye concentration 2×10^{-5} M).

through common ion effect resulting in an increased and facilitated uptake onto resin 2 surface [61]. These two factors are responsible for enhanced adsorption behavior of resin 2 toward selected azo dyes.

3.2.3. *Role of electrolytes on the adsorption of azo dyes*

No doubt, electrolytes play an important role in dye removal by affecting the solution chemistry. To investigate the effect of ionic strength, adsorption experiments were carried out in the presence of four different electrolytes of 0.2 M concentrations: NaOH, Na_2CO_3, Na_2SO_4, and $NaHCO_3$. It can be observed from (Fig. 3(b)) that RB-5 dye removal efficiency of resin 2 remain almost same in the presence of Na_2SO_4. While its capacity decreases with the addition of other electrolytes. The electrolytes affect in the order of $NaHCO_3 < Na_2CO_3 < NaOH$. It means Na_2SO_4 increases adsorption by increasing salting out itself and due to common ion effect. The decline in dye removal efficiency may be due to the disturbance of pH of the solution by these electrolytes. Likewise, DB-38 dye removal efficiency of resin 2 also increases by the addition of NaOH and Na_2SO_4. This salting out as well as common ion effect stimulates the adsorption of DB-38 azo dye. On the other hand, $NaHCO_3$ and Na_2CO_3 decrease the efficiency of DB-38 azo dye removal.

3.2.4. *pH effects on azo dyes adsorption*

pH is one of the most important variables affecting factor that influences not only surface charges of adsorbent but also dye solution chemistry, i.e. the degree of ionization of dye molecule present in solution along with the dissociation of functional groups at active sites of the adsorbent [62]. In this study, influence of pH on adsorption behavior of the selected azo dyes was investigated with different adsorbents such as pure XAD-4 (1), (III), and resin 2 as represented in (Fig. 4(a)). Observations were carried out at different pH (3,5,7,9, and 11) with a contact time of 1 h. The results indicate that the maximum adsorption 95% of RB-5 onto the resin 2 occur at pH 3. Thus acidic pH was more favorable for adsorption of RB-5 onto resin 2. Contrary to this, RB-5 dye removal efficiency of resin 2 reduced to 60% at basic pH, i.e. 11. That means, by increasing the pH, adsorption of RB-5 azo dye decreased dramatically. Furthermore, at basic pH, number of negatively charged sites increase and number of positively charged sites decrease as well. A negatively charged surface site of resin 2 does not favor adsorption of dye anions due to electrostatic repulsion. Moreover, adsorption efficiency of resin 2 over all was found greater than 1 and (III) may be due to the greater surface area and appropriate projection of binding sites of calixarene moiety in resin 2.

As pH has a great contribution in separation science, hence influence of the initial solution pH on percent adsorption of DB-38 dye onto resin 2 revealed in (Fig. 4(b)) which shows significant adsorption of DB-38 azo dye occurs in a wide range of pH 3 to pH 11. As it has been noticed that adsorption of DB-38 azo dye increased continually with the rise of pH, while DB-38 adsorbed maximally 91% at pH 11. At acidic pH, positively charged H^+ ions are present in excess that competes with the dye cation for adsorption sites. Because at lower pH values due to electrostatic repulsion of positively charged surface sites of resin 2 do not favor the adsorption of dye cations. On the other hand, as the pH of the system increased, (3–11) the number of positively charged available sites

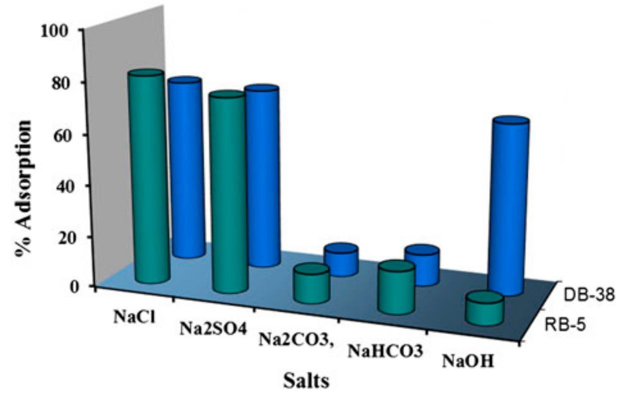


Fig. 3(b). Role of different electrolytes in the adsorption of RB-5 and DB-38 azo dyes (50 mg resin 2, 60 min of contact time and 10 mL of dye concentration 2×10^{-5} M).

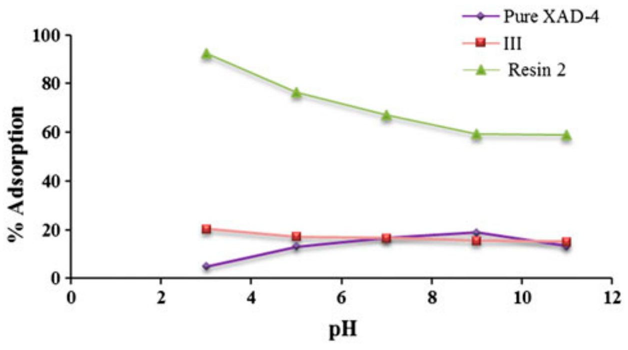


Fig. 4(a). pH effect on the adsorption of RB-5 (50 mg of resin 2, 1 h of contact time, 0.2 M of NaCl and 10 mL of dye concentration 2×10^{-5} M).

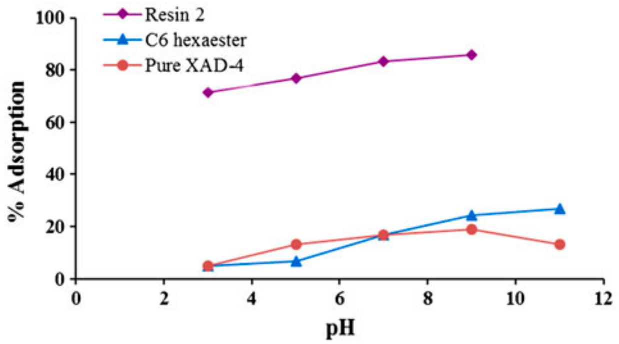


Fig. 4(b). pH effect on the sorption of DB-38 (50 mg of resin 2, 1 h of contact time, 0.2 M of NaCl and 10 mL of dye concentration 2×10^{-5} M).

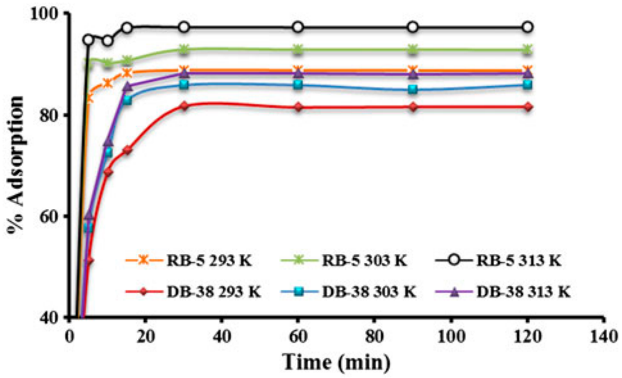


Fig. 5. Adsorption curves of RB-5 and DB-38 azo dyes onto resin 2 as a function of shaking time at different temperatures, i.e. 293–313 K.

decreases while the number of negatively charged sites increases. In this phenomenon, negatively charged sites of ester functionality at lower rim of the calix[6]arene in resin 2 show binding ability toward the sodium ions of DB-38 azo dye. The negatively charged sites favor the adsorption of dye cation due to electrostatic attraction with metal ion coordination between resin 2 and dye molecule. This implies an ion-pair extraction mechanism in which Na^+ ions coordinates with negatively charged oxygen atoms of ester functional group, i.e. anionic sites resin 2. While rest of the azo dye molecule inserts into the hydrophobic calix[6]arene cavity of resin 2.

3.2.5. Optimum shaking time

The adsorption efficiency of resin 2 for selected azo dyes as a function of shaking time was carried out at different temperatures (293–313 K); as shown in (Fig. 5). It has been found that adsorption capacity of resin 2 increases with the rise of temperature and shaking time. It indicates that the adsorption process is temperature dependent. For RB-5, the equilibrium was established within 5 min at different temperatures and only minor increment in percent adsorption was observed up to 20 min. While for DB-38 azo dye, 15 min were quite sufficient for equilibrium to be obtained and slight enhancement was also noticed in adsorption up to 30 min. Thus, further experimental work was carried out for 1 h of shaking time in order to avoid any error.

3.2.6. Adsorption isotherms

Design and analysis of adsorption behavior through isotherm models is the most significant piece of information to understand surface chemistry. Different parameters of these equilibrium models demonstrate the interaction of adsorbate and adsorbent matrix. It often provides some insight into the surface properties and affinity of adsorbent to adsorbate and help to identify adsorption mechanism. In the present work, the adsorption efficiency of resin 2 for selected azo dyes has been estimated by means of three equilibrium models, i.e. Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm equations.

The adsorbate ions chemically adsorbed on the predetermined number of well-defined sites. It suggests monolayer adsorption on an energetically homogeneous surface without mutual interactions between the adsorbate molecules [63]. The Langmuir isotherm was tested to evaluate the adsorption behavior of azo dyes onto resin 2; Eq. (1) is the linear form of Langmuir isotherm as given below:

$$\left(\frac{C_e}{C_{ads}}\right) = \left(\frac{1}{Qb}\right) + \left(\frac{C_e}{Q}\right) \tag{1}$$

A plot of (C_e/C_{ads}) vs. C_e exhibits a straight line with slope of ($1/Q$) and intercept ($1/Q_b$).

The essential factor in terms of a dimensionless constant is a separation factor "R_L" can be estimated from the value of Langmuir constant b which describes the type of isotherm and is defined by applying Eq. (2).

$$R_L = \frac{1}{(1 + b\,C_i)} \tag{2}$$

The value of R_L assess the favorability and unavoidability of adsorption process which can be justify as favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), and linear ($R_L = 1$).

The comparison of correlation coefficients (R^2) for RB-5 and DB-38 indicates that the Langmuir adsorption model yields a better fit for the experimental data of RB-5 as compared to DB-38. It proposes the monolayer coverage of RB-5 dye on the surface of resin 2. The value of Q mmol/g and the Langmuir constant b mol/L has been calculated which are also given in Table 1.

The Freundlich isotherm model is in empirical expression describing the dispersion of active sites and their energies, characteristic of heterogeneous surface and infinite surface coverage [64]. Eq. (3) is a linear form of this isotherm

$$\ln C_{\mathrm{ads}} = \ln A + \frac{1}{n} \ln C_{\mathrm{e}} \tag{3}$$

The values multilayer adsorption capacity A and $1/n$ have been calculated from the intercept and slope of graph by plotting $\ln C_{\mathrm{ads}}$ vs. $\ln C_{\mathrm{e}}$.

From the data correlation coefficients (R^2) value of RB-5 and DB-38 indicates that these dyes have exactly same experimentally data for Freundlich adsorption model. The constant values of $1/n$ and A was calculated and is given in Table 1 where values n suggests the favorability of Freundlich isotherm model.

The D–R isotherm is a more general model which helps to differentiate physico-chemical nature of adsorption [65]. It assumes heterogeneity of energies over the surface. The linear form of D–R equation is represented as:

$$\ln C_{\mathrm{ads}} = \ln X_{\mathrm{m}} - \beta\varepsilon^2 \tag{4}$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_{\mathrm{e}}}\right) \tag{5}$$

where R is the gas constant in kJ/mol K and T is the temperature in Kelvin.

The value of E can be calculated from the value of constant b by applying of D–R isotherm model Eq. (6) as follows

$$E = \frac{1}{\sqrt{-2\beta}} \tag{6}$$

where β is related to mean energy of adsorption and described as free energy for the transfer of one mole of dye molecule from infinity to the surface of resin 2. A plot of $\ln C_{\mathrm{ads}}$ vs. ε^2 gives a straight line. The saturation limit X_{m} may represent total specific micropore volume of the resin 2. Most importantly, magnitude of E (free energy) plays a significant role in determining the type of adsorption. If the value lies between 0 and 8 kJ/mol, it implies physiosorption. While value lies in between 8 and 16 kJ/mol, the mode of adsorption can be explained by ion exchange mechanism or chemisorption. Hence, in this case, the value of E is determined as 9.449 kJ/mol for RB-5 and 10.885 kJ/mol for DB-38. This illustrates that adsorption process of both azo dyes onto resin 2 follow chemisorption mechanism and explains the applicability of experimental data for the D–R isotherm.

Moreover, on the basis of correlation coefficient (R^2), the adsorption process of these dyes by resin 2 described in Table 1. It has been noticed that the order of favorability on the basis of R^2 value for RB-5 and DB-38 is as: Langmuir (0.99) and (0.98), Freundlich (0.98) and (0.98), D–R (0.99) and (0.99), respectively. Therefore, each isotherm has specific qualities to elucidate the potency of resin 2 for these azo dyes adsorption. From these observations, it may be concluded that higher adsorption capacity of resin 2 for RB-5 and DB-38 azo dyes is in good agreement with Langmuir and D–R isotherm models which specify the monolayer coverage of RB-5 and DB-38 azo dyes through ion-exchange mechanism onto energetically homogeneous surface of resin 2.

3.2.7. Adsorption kinetics

In order to analysis the kinetics for adsorption of RB-5 and DB-38 azo dyes onto resin 2, the experimental data was employed to different kinetic equations such as Lagergren pseudo-first-order, pseudo-second-order equation [66,67] and diffusion models [68,69].

Table 1
Langmuir, Freundlich and D–R characteristic constants for RB-5 and DB-38 azo dyes

Azo dye	Langmuir				Freundllich				D–R		
	Q (mmol/g)	$b \times 10^4$ L/mol	R_{L}	R^2	A (mol/g)	n	$1/n$	R^2	E	X_{m}	R^2
RB-5	1,485.66	0.60	0.99	0.99	856.84	1.68	0.59	0.98	9.44	0.01	0.99
DB-38	0.11	7.23	0.1–0.99	0.98	5,908.80	1.84	0.54	0.98	10.88	136.79	0.99

The pseudo-first-order equation can be expressed as,

$$\ln\,(q_{\mathrm{e}} - q_{\mathrm{t}}) = \ln q_{\mathrm{e}} - K_{\mathrm{t}} \tag{7}$$

Experimental data also evaluated by utilizing the pseudo-second-order equation and is expressed as follows:

$$d_{\mathrm{q}}\; d_{\mathrm{t}} = K_2(q_{\mathrm{e}} - q_{\mathrm{t}})^2 \tag{8}$$

For same boundary conditions the integrated form of Eq. (8) becomes Eq. (9).

$$\frac{1}{q_{\mathrm{t}}} = \left(\frac{1}{k_2 q_{\mathrm{e}}^2}\right) + \left(\frac{1}{q_{\mathrm{e}}}\right) t \tag{9}$$

Kinetic parameters along with correlation coefficients values of kinetic models are given in Table 2. It has been considered that values of correlation coefficients R^2 of the pseudo-first-order kinetic model at various temperatures, i.e. 293, 303, and 313 K for RB-5 and DB-38 azo dyes onto resin 2 do not describe the adsorption kinetics of this system. While in the case of pseudo-second-order model correlation coefficients R^2 values explains this adsorption behavior significantly and these selected azo dyes follows pseudo-second-order kinetic model. The pseudo-second-order kinetic model is based on the assumption that the rate limiting step may be chemical adsorption involving an electrostatic interaction between adsorbent surface functional groups and adsorbate molecules. Furthermore, pseudo-second-order kinetic model suggests that adsorption phenomenon of selected azo dyes is purely chemical in nature which is supported by electrostatic interactions between resin 2 and dyes molecules.

3.2.8. Adsorption mechanism

The pseudo-first and pseudo-second-order kinetic models could not identify the diffusion mechanism and the kinetic results were then analyzed by using the diffusion models.

The Reichenberg equation was utilized to analyze the adsorption of azo dyes RB-5 and DB-38 took place through either film interaction or intrapartical diffusion mechanism; the Reichenberg equation is given as under:

$$Q = 1 - 6e - Bt/\pi^2 \tag{10}$$

$$B_{\mathrm{t}} = -0.4977 - \ln(1 - Q) \tag{11}$$

The plot of B_{t} vs. time t follows the linearity. For adsorption, straight line of this plot is employed to differentiate between external transport (film diffusion) and transport-controlled rates (intraparticle diffusion). In case of both dyes, the results clearly indicates that at different temperatures, all lines are linear and do not pass through the origin which suggests that adsorption of these azo dyes onto resin 2 took place via film diffusion which is a rate-limiting process.

The kinetics of adsorption was also examined by using Morris–Weber equation

$$q_{\mathrm{t}} = R_{\mathrm{d}}\sqrt{t} \tag{12}$$

where q_{t} is the sorption concentration of azo dyes that at time t and R_{d} is the rate constant of intraparticle transport. The q_{t} (mol/g) was plotted against $\sqrt{t}$.

From slope of the plot, values of rate constant of intrapartical transport (R_{d}) were estimated for RB-5 azo dye as 0.622, 0.771, and 0.944 mol/g/min with the correlation coefficients 0.947, 0.959, and 0.969 and for

Table 2
Comparisons of pseudo-first-order and pseudo-second-order kinetic models

Pseudo-first-order kinetic model				Pseudo-second-order kinetic model		
	K_1 (1/min)	q_{e} (mol/g)	R^2	K_1 (1/min)	q_{e} (mol/g)	R^2
	RB-5 dye					
20	0.11	2.36	0.81	3.44×10^{-11}	9.46×10^{-2}	0.99
30	0.84	1.99	0.42	4.21×10^{-12}	8.95×10^{-5}	1
40	1.54	1.36	0.22	5.03×10^{-11}	9.15×10^{-5}	1
	DB-38 dye					
20	891.34	95.23	0.48	7.96×10^{-5}	3.41×10^{-13}	0.99
30	703.83	85.47	0.43	5.33×10^{-5}	8.33×10^{-5}	0.99
40	539.32	75.18	0.44	6.10×10^{-5}	8.57×10^{-5}	0.99

DB-38 found as 0.062, 0.064, 0.072 mol/g/min with the correlation coefficients 0.835, 0.745, and 0.755, respectively from 293 to 313 K. However, linear plots in this study also do not pass through the origin. This indicates that for adsorption of selected azo dyes onto resin 2 intraparticle diffusion is not only the rate limiting step and some degree of boundary layer also controls the process.

3.3. Thermodynamics of adsorption

The thermodynamic parameters including change in the enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) are the actual indicators for practical application of a process which can explain the adsorption mechanism [70]. Thus, the effect of temperature on adsorption of RB-5 and DB-38 azo dyes onto resin 2 was explored at different temperatures (i.e. 298, 308, and 318 ± 1 K). It has been found that adsorption capacity (q_e) also increases with increase in temperature. The plot of ln K_c vs. $1/t$ gives a straight line with correlation coefficients of (R^2) 0.99 for RB-5 and DB-38 dyes as shown in (Fig. 6).

The thermo dynamic parameters ΔH, ΔS, and ΔG were calculated from the slope and intercept of the linear plot of ln (q_e/C_e) vs. $1/t$ by using the following Eqs. (13 and 14).

$$\ln Kc = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{13}$$

$$\Delta G = -RT \ln Kc \tag{14}$$

From Fig. 5, it has been concluded that the percent adsorption increases rapidly with increasing the temperature from at 293, 303, and 313 K. The increase in adsorption capacity of resin 2 was attributed to the enlargement of pore size and activation of the resin 2 surface with temperature. Besides, this rise in temperature increases the mobility of large dye ions and reduces the swelling effect, thus, enabling the large dye molecule to penetrate further [71]. The numerical values of ΔH and ΔS were and ΔG was determined from Eqs. (13) and (14). These values obtained are listed in Table 3. The ΔG value is negative as expected for a spontaneous process under the applied conditions confirms that these azo dyes adsorbed spontaneously onto the surface of resin 2. Endothermic nature of adsorption can be analyzed form positive value of ΔH. Values of ln K_c for both dyes increases at different temperatures, i.e. for RB-5 (2.07, 2.58, and 2.97 and for DB-38 1.49, 1.80, 2.01 at 293, 303, and 313 K, respectively) with increase of temperature showing that both azo dyes adsorbed endothermally onto the surface of resin 2. It can be suggested that the driving force for adsorption process is an entropy effect and slightly positive value of entropy (ΔS) implies the increased degree of freedom at the solid/solution interface during the adsorption of RB-5 and DB-38 dyes onto resin 2.

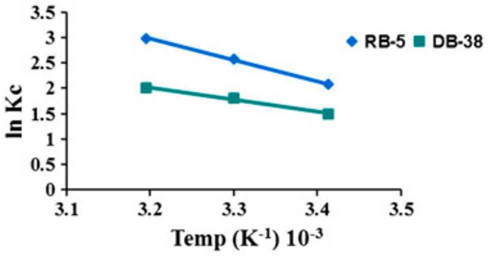


Fig. 6. Effect of temperature on the adsorption of RB-5 and DB-38 azo dyes onto resin 2.

3.4. Field applications of resin 2

Dye removal efficiency of resin 2 was evaluated by carrying out field study of real wastewater samples containing azo dyes. Batch experiments were performed with 50 mg of resin and 10 mL of real sample containing these dyes. The mixture of resin 2 and waste effluent was shaken at 160 rpm for 1 h at 30°C. The remaining concentration of azo dyes was determined before and after treatment of dyes wastewater with resin 2 through spectrophotometerically at their respective specific wavelengths, i.e. 597 and 592 nm. The obtained results are summarized in Table 4.

From results, it is quite clear that lower concentration of azo dyes remained in waste effluents after the treatment with resin 2. Besides this, resin 2 also decreases the other important parameters like pH, TDS, conductivity, and salinity of real water samples as shown in Table 5. It has been concluded that resin 2 is an efficient adsorbent for the removal of selected azo dyes which can be successfully employed for the purification of aqueous environment.

3.5. Comparison of azo dyes adsorption with other adsorbents

A comparative evaluation of adsorbent capacity of resin 2 for the adsorption of RB-5 and DB-38 azo dyes with various types of adsorbents reported in literature was made. The maximum adsorption capacity Q of resin 2 for RB-5 at pH 3 has been evaluated as 1,485.66 mmol/g while for DB-38 at

Table 3
Thermodynamic parameters for adsorption of RB-5 and DB-38 azo dyes onto resin 2

Azo dye	ΔH (kJ/mol)	ΔS (kJ/mol K)	ΔG (kJ/mol)		
			293 K	303 K	313 K
RB-5	0.0384	0.135	−7.74 $\ln K_c = 2.07$	−6.50 $\ln K_c = 2.58$	−5.05 $\ln K_c = 2.97$
DB-38	0.019	0.080	−5.24 $\ln K_c = 1.49$	−4.55 $\ln K_c = 1.80$	−3.64 $\ln K_c = 2.01$

Table 4
Azo dyes concentration in waste water samples before and after treatment with resin 2

S. No	Conc. before treatment	Conc. after treatment	% Removal
1	1.40×10^{-4}	5.01×10^{-5}	76.11
2	3.70×10^{-5}	9.50×10^{-6}	69.32
3	2.90×10^{-5}	1.30×10^{-5}	49.64
4	3.20×10^{-5}	9.00×10^{-6}	71.12

Table 5
Comparison of pH, TDS, conductivity, and salinity of waste water samples by using resin 2

S. No	Before treatment				After treatment			
	pH	TDS (mg/L)	Conductivity (μS/cm)	Salinity	pH	TDS (mg/L)	Conductivity (μS/cm)	Salinity
1	9.2	437	1,663.5	2.1	7.4	230	362.5	0
2	9.5	261	1,800	0.5	8.8	53	527	0
3	10.5	136	1,445	0.9	7.3	52.6	625	0.2
4	9.7	178.5	1,121	3.0	7.1	25	320	0.4

pH 9 the adsorption capacity has been found as 1,125.36 mmol/g. Adsorption capacity Q of Karbon aktif (cangkang bijiketapang) [72] for DB-38 dye has only 74.54 mg/g adsorption capacity which is very low as compared to the present work. Similarly, adsorption capacities of different materials like zeolite, sapiolite [73], biomass [74], nanospinel $ZnCr_2O_4$ [75] thermophilic cyanobacterium phormidium sp. [76], mesoporous carbon [77], and Corynebacterium glutamicum [78] for RB-5 is 60–600 mg/g, but comparatively, resin 2 has very high Q value, i.e. 1,485.66 mg/g. From the data, it has been concluded that the adsorption capacity of resin 2 is relatively high when compared with other reported adsorbent materials. Therefore, it has been concluded that very high adsorption capacity of resin 2 is due to the presence of calixarene moiety. This calix[6]arene framework provides appropriate binding sites along with greater surface area in resin 2.

4. Conclusion

This study highlighted the main features of synthesis and application of newly synthesized resin 2 for adsorption of selected azo dyes RB-5 and DB-38 from aqueous media. Resin 2 was characterized by basic as well as advanced instrumental techniques. Batch mode was used to optimize some experimental parameters, i.e. pH, adsorbent dose, contact time, and temperature. Adsorption of both selected azo dyes is pH dependent. The equilibrium, kinetic, and thermodynamic studies were also carried out to understand the adsorption process. Isotherm models validation suggests that both azo dyes RB-5 and DB-38 tend to follow Langmuir and D–R isotherm models as compared to the Freundlich isotherm. Kinetic studies for both dyes can be best explained by pseudo-second-order model. Thermal studies clarify that adsorption process is endothermic as well as spontaneous in nature. Noticeable high adsorption capacity of resin 2 in comparison to other materials made it a promising and competent adsorbent for dyes removal from aqueous media. Moreover, the field studies also support the resin 2 as an effective adsorbent for the elimination of azo dyes. Additionally, it also reduces other water quality parameters like pH, TDS, conductivity, and salinity near to the drinking water. Hence, results of this study reveals that resin 2 has high removal capacity to adsorb RB-5 and DB-38 azo dyes from the wastewater. This highly recommends that resin 2 can be efficiently used for the purification of aqueous environment.

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References

[1] T. Deveci, A. Unyayar, M.A. Mazmanci, Production of remazol brilliant blue R decolourising oxygenase from the culture filtrate of Funalia Trogii ATCC 200800, J. Mol. Catal. B: Enzym. 30 (2004) 25–32.

[2] R.G. Saratale, G.D. Saratale, J.S. Chang, S.P. Govindwar, Bacterial decolorization and degradation of azo dyes: A review, J. Taiwan. Inst. Chem. Eng. 42 (2011) 138–157.

[3] H. Zollinger, Color Chemistry: Synthesis Properties and Applications of Organic Dyes and Pigments, second revised ed., VCH, New York, NY. (1991) 150–250.

[4] W.Z. Tang, Z. Zhang, H. An, M.O. Quintana, D.F. Torres, TiO_2/UV photodegradation of azo dyes in aqueous solutions, Environ. Technol. 18 (1997) 1–12.

[5] D.C. Kalyani, A.A. Telke, R.S. Dhanve, J.P. Jadhav, Ecofriendly biodegradation and detoxification of Reactive Red 2 textile dye by newly isolated pseudomonas sp. SUK1, J. Hazard. Mater. 163 (2009) 735–742.

[6] I. Mustafa, T.S. Delia, Monitoring of toxicity and intermediates of C.I. direct black 38 azo dye through decolorization in an anaerobic/aerobic sequential reactor system, J. Hazard. Mater. 114 (2004) 29–39.

[7] A. Gnanamani, M. Bhaskar, R. Ganeshjeevan, R. Chandrasekar, G. Sekaran, S. Sadulla, G. Radhakrishnan, Enzymatic and chemical catalysis of xylidine ponceau 2R and evaluation of products released, Proc. Biochem. 40 (2005) 3497–3504.

[8] M.S. Usha, B. Sasirekha, R.B. Bela, S. Devi, C. Kamalini, G.A. Manasa, P.M. Neha, Optimization of Reactive Black 5 dye and Reactive Red 120 dye degradation, J. Chem. Pharmaceutical Res. 3 (2006) 450–457.

[9] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: Influence of solubility and bioavailability, Toxicol. Lett. 151 (2004) 203–210.

[10] R.P. Pohanish, Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens. sixth ed., WAP, Amsterdam, 2012, pp. 125–127.

[11] B.W. Manning, C.E. Cerniglia, T.W. Federle, Metabolism of the benzidine based azo dye DB 38 by human intestinal microbiota, Appl. Environ. Microbiol. 50 (1985) 10–15.

[12] E. Akceylan, M. Bahadir, M. Yilmaz, Removal efficiency of a calix[4]arene based polymer for water soluble carcinogenic direct azo dyes and aromatic amines, J. Hazard. Mater. 162 (2009) 960–966.

[13] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: Status Review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters, Dyes Pigm. 61 (2004) 121–139.

[14] Y. Shengquan, W. Hui, Z. Chaohua, H. Fu, Separation of carcinogenic aromatic amines in the food colourants plant wastewater treatment, Desalination 222 (2008) 294–301.

[15] European Commission, 2002/61/EC, Off. J. Eu. Commun 15 (2002) 15–18.

[16] B. Karagoz, G. Bayramoglu, B. Altintas, N. Bicak, M.Y. Yakup Arica, Amine functional monodisperse microbeads via precipitation polymerization of N-vinyl formamide: Immobilized laccase for benzidine based dyes degradation, Bioresour. Technol. 102 (2011) 6783–6790.

[17] A. Mittal, Removal of the dye Amaranth from waste water using hen feathers as potential adsorbent, Electron. J. Environ. Agric. Food Chem. 5 (2006) 1296–1305.

[18] J. Mittal, V. Thakur, A. Mittal, Batch removal of hazardous azo dye Bismark Brown R using waste material hen feather, Ecol. Eng. 60 (2013) 249–253.

[19] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desalin. Water Treat. 52 (2014) 4508–4519.

[20] G. Sharma, M. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of Hibiscus cannabinus fiber by graft copolymerization: Application for dye removal, Desalin. Water Treat. (2014) 1–8. doi:10.1080/19443994.2014.904822.

[21] A. Mittal, V. Thakur, J. Mittal, H. Vardhan, Process development for the removal of hazardous anionic azo dye congo red from wastewater by using hen feather as potential adsorbent, Desalin. Water Treat. 52 (2014) 227–237.

[22] A. Mittal, L. Kurup, Column operations for the removal and recovery of a hazardous dye ACID RED-27 from aqueous solutions using waste material-bottom ash and de-oiled soya, Ecol. Environ. Conserv. 13 (2006) 181–186.

[23] G. Crini, Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol. 97 (2006) 1061–1085.

[24] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative, Bioresour. Technol. 77 (2001) 247–255.

[25] L. Zheng, Y. Su, L. Wang, Z. Jiang, Adsorption and recovery of methylene blue from aqueous solution through ultrafiltration technique, Sep Purif. Technol. 68 (2009) 244–249.

[26] A. Geethakarthi, B.R. Phanikumar, Industrial sludge based adsorbents/industrial by products in the

removal of reactive dyes: A review, Int. J. Water Resour. Environ. Eng. 3 (2011) 1–9.

[27] H. Daraei, A. Mittal, M. Noorisepehr, F. Daraei, Kinetic and equilibrium studies of adsorptive removal of phenol onto eggshell waste, Environ. Sci. Pollut. Res, 20(7), 4603–4611.

[28] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies, Desalin. Water Treat. (2013) 1–7. doi:10.1080/19443994.2013.837011.

[29] H. Daraei. A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto biosorbent eggshell membrane: Experimental and theoretical approaches, Desalin. Water Treat. 52 (2014) 1307–1315.

[30] M. Naushad, A. Mittal, M. Rathore, V. Gupta, Ion-exchange kinetic studies for Cd(II), Co(II), Cu(II), and Pb(II) metal ions over a composite cation exchanger, Desalin. Water Treat. (2014) 1–8. doi:10.1080/19443994.2014.904823.

[31] I.B. Solangi, S. Memon, M.I. Bhanger, An excellent fluoride sorption behavior of modified Amberlite resin, J. Hazard. Mater. 176 (2010) 186–192.

[32] A.A. Bhatti, A.A. Bhatti, I.B. Solangi, S. Memon, Pb^{2+} adsorption behavior of calix[4]arene based merrifield resin. Desalin. Water Treat. 51 (2013) 4666–4674.

[33] K.K.H. Choy, G. McKay, J.F. Porter, Sorption of acid dyes from effluents using activated carbon, Resour. Conserv. Recycl. 27 (1999) 57–71.

[34] D.A. Fungaro, M. Yamaura, T.E.M. Carvalho, Adsorption of anionic dyes from aqueous solution on zeolite from fly ash-iron oxide magnetic, J. Mol. Sci. 2 (2011) 305–316.

[35] M. Bagane, S. Guiza, Removal of a dye from textile effluents by adsorption, Ann. Chim. Sci. Mater. 25 (2000) 615–625.

[36] G. Mc Kay, H.S. Blair, J.R. Gardner, Rate studies for the adsorption of dyestuffs onto Chitin, J. Colloid. Interface Sci. 95 (1983) 108–119.

[37] R.S. Juang, R.L. Tseng, F.C. Wu, S.H. Lee, Adsorption behavior of reactive dyes from aqueous solutions on chitosan, J. Chem. Technol. Biotechnol. 70 (1997) 391–399.

[38] F. Delval, G. Crini, N. Morin, J. Vebrel, S. Bertini, G. Torri, The sorption of several types of dye on cross-linked polysaccharides derivatives, Dyes Pigm. 53 (2002) 79–92.

[39] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[40] T. Robinson, B. Chandran, P. Nigam, Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw, Water Res. 36 (2002) 2824–2830.

[41] S. Sadaf, H.N. Bhatti, Batch and fixed bed column studies for the removal of Indosol Yellow BG dye by peanut husk, J. Taiwan Inst. Chem. Eng. 45 (2014) 541–553.

[42] S. Noreen, H.N. Bhatti, S. Nausheen, S. Sadaf, M. Ashfaq, Batch and fixed bed adsorption study for the removal of Drimarine Black CL-B dye from aqueous solution using a lignocellulosic waste: A cost affective adsorbent, Ind. Crops Prod. 50 (2013) 568–579.

[43] S. Sadaf, H.N. Bhatti, S. Ali, K. Rehman, Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: Batch and column study, Desalin. Water Treat. 52 (2014) 184–198.

[44] S. Nausheen, H.N. Bhatti, S. Sadaf, Z. Farrukh, S. Noreen, Equilibrium modeling of removal of Drimarine Yellow HF-3GL dye from aqueous solutions by low cost agricultural waste, J. Chem. Soc. Pakistan 36 (2014) 177–190.

[45] C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani, K. Ranganathan, Removal of dyes from aqueous solutions by cellulosic waste orange peel, Bioresour. Technol. 57 (1996) 37–43.

[46] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, S. Memon, Synthesis and application of *p-tert*-butylcalix[8]arene immobilized material for the removal of azo dyes, J. Hazard. Mater. 186 (2011) 651–658.

[47] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, S. Memon, A highly efficient calix[4]arene based resin for the removal of azo dyes, Desalination 268 (2011) 83–89.

[48] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, S. Memon, Synthesis and application of calix[4]arene based resin for the removal of azo dyes, J. Hazard. Mater. 172 (2009) 234–239.

[49] D. Chatterjee, V.R. Patnam, A. Sikdar, S.K. Moulik, Removal of some common textile dyes from aqueous solution using fly ash, J. Chem. Eng. Data 55 (2010) 5653–5657.

[50] A.A. Bhatti, M.A. Kamboh, I.B. Solangi, S. Memon, Synthesis of calix[6]arene based XAD-4 material for the removal of reactive blue 19 from aqueous environment, J. Appl. Poly. Sci. 130 (2013) 676–685.

[51] S. Memon, M. Yilmaz, Biscalixarenes: Synthesis and investigation of the extraction behavior of biscalix[4]arene derivatives in a two-phase extraction system, Sep. Sci. Technol. 36 (2001) 473–486.

[52] M. Tabakci, S. Memon, B. Sap, D.M. Roundhill, M. Yilmaz, A calix[4]arene derived dibenzonitrile receptor modified at its "lower rim" by a polymerizable group, Pure. Appl. Chem. 41 (2004) 811–825.

[53] M. Tabakci, S. Memon, M. Yilmaz, D.M. Roundhill, Synthesis and evaluation of extraction ability of calix[4]-crown-6 cone conformer and its oligomeric analogue, React. Funct. Polym. 58 (2004) 27–34.

[54] S. Memon, A. Yilmaz, D.M. Roundhill, M. Yilmaz, Synthesis of polymeric calix[4]arene dinitrile and diamino-derivatives: Exploration of their extraction properties towards dichromate anion, J. Macromol. Sci. Part A Pure. Appl. Chem. 41 (2004) 433–447.

[55] M.A. Kamboh, I.B. Solangi, S.T.H. Sherazi, S. Memon, Sorption of congo red onto p-tert-butylcalix[4]arene based silica resin, J. Iran. Chem. Soc. 8 (2011) 272–279.

[56] M.A. Kamboh, A.A. Bhatti, I.B. Solangi, S.T.H. Sherazi, S. Memon, Adsorption of direct black-38 azo dye on p-tert-butylcalix[6]arene immobilized material, Arab. J. Chem. 7 (2014) 125–131.

[57] C.D. Gutsche, M. Iqbal, D. Stewart, Calixarenes 19 syntheses procedures for p-tert-butylcalix[4]arene, J. Org. Chem. 51 (1986) 742–745.

[58] C.D. Gutsche, L.G. Lin, Calixarenes 12, Tetrahedron 42 (1986) 1633–1640.

[59] K. Iwamoto, S. Shinkai, Synthesis and ion selectivity of all conformational isomers of tetrakis[(ethoxycarbonyl)methoxy]calix[4]arene, J. Org. Chem. 57 (1992) 7066–7073.

[60] I.B. Solangi, S. Memon, M.I. Bhanger, Synthesis and application of a highly efficient tetraester calix[4]arene based resin for the removal of Pb^{2+} from aqueous environment, Anal Chim Acta. 638 (2009) 146–153.

[61] G. Crini, Studies on adsorption of dyes on beta-cyclodextrin polymer, Bioresour. Technol. 90 (2003) 193–198.

[62] E. Errais, J. Duplay, F. Darragi, I. M'Rabet, A. Aubert, F. Huber, G. Morvan, Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, Desalination 275 (2011) 74–81.

[63] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[64] H. Freundlich, Colloid and Capillary Chemistry, Methuen, London, 1926, pp. 397–414.

[65] M.Polanyi, Theories of the adsorption of gases. A general survey and some additional remarks introductory paper to section III, Trans. Faraday. Soc. 28 (1932) 316–333.

[66] E. Haribabu, Y.D. Upadhya, S.N. Upadhyay, Removal of phenols from effluents by fly ash, Int. J. Environ. Stud. 43 (1993) 169–176.

[67] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Proc. Biochem. 34 (1999) 451–465.

[68] D. Reichenberg, Properties of ion-exchange resins in relation to their structure III. Kinetics of exchange, J. Am. Chem. Soc. 75 (1953) 589–597.

[69] W.J. Weber Jr, J.C. Morris, Kinetics of adsorption on carbon from solutions, J. Sanit. Eng. Div. Proceed. Am. Soc. Civil Eng. 89 (1963) 31–59.

[70] G.Z. Memon, M.I. Bhanger, M. Akhtar, The removal efficiency of chestnut shells for selected pesticides from aqueous solutions, J. Colloid. Interface Sci. 315 (2007) 33–40.

[71] Y. Liu, Y.J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol. 61 (2008) 229–242.

[72] M. Ambas, Final Project Report, Department of Chemical Engineering, Polytechnic Samarinda, 2010.

[73] O. Ozdemir, B. Armagan, M. Turan, M.S. Çelik, Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals, Dyes Pigm. 62 (2004) 49–60.

[74] Z. Aksu, S. Tezer, Equilibrium and kinetic modelling of biosorption of Remazol Black B by Rhizopus arrhizus in a batch system: Effect of temperature, Proc. Biochem. 36 (2000) 431–439.

[75] M. Yazdanbakhsh, I. Khosravi, E.K. Goharshadi, A. Youssefi, Fabrication of nanospinel $ZnCr_2O_4$ using sol–gel method and its application on removal of azo dye from aqueous solution, J. Hazard. Mater. 184 (2010) 684–689.

[76] Z. Aksu, S. Ertuğrul, G. Dönmez, Single and binary chromium(VI) and Remazol Black B biosorption properties of phormidium Sp, J. Hazard. Mater. 168 (2009) 310–318.

[77] W. Tanthapanichakoon, P. Ariyadejwanich, P. Japthong, K. Nakagawa, S.R. Mukai, H. Tamon, Adsorption–desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires, Water Res. 39 (2005) 1347–1353.

[78] K. Vijayaraghavan, Y.S. Yun, Utilization of fermentation waste (Corynebacterium glutamicum) for biosorption of Reactive Black 5 from aqueous solution, J. Hazard. Mater. 141 (2007) 45–52.