



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



SPECIAL ISSUE: ENVIRONMENTAL CHEMISTRY

Adsorption of direct black-38 azo dye on *p*-tert-butylcalix[6]arene immobilized material

Muhammad Afzal Kamboh ^{a,b}, Asif Ali Bhatti ^b, Imam Bakhsh Solangi ^c,
S.T.H. Sherazi ^b, Shahabuddin Memon ^{b,*}

^a National Center of Excellence in Analytical Chemistry, University of Sindh, Jamshoro 76080, Pakistan

^b Department of Chemistry, Kohat University of Science & Technology, Kohat, KhyberPakhtunkhwa, Pakistan

^c Dr M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Pakistan

Received 26 February 2013; accepted 26 June 2013

Available online 9 July 2013

KEYWORDS

Calixarene;
Immobilization;
Silica resin;
Direct azo dye;
Solid-phase extraction;
Batch-wise sorption

Abstract The present study demonstrates the adsorption of the direct black-38 (DB-38) azo dye on potential and newly synthesized *p*-tert-butylcalix[6]arene based silica resin (**4**). Resin **4** was synthesized *via* the modification of pure silica **1** as **2** followed by the immobilization of *p*-tert-butylcalix[6]arene (**3**) onto modified silica (**2**). It was characterized by using different analytical techniques such as FT-IR, scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA). The effect of adsorbent dosage, pH and the electrolyte effect on the removal of the DB-38 azo dye were evaluated through batch wise adsorption experiments. Maximum adsorption of 91% was achieved at pH 9.0. The textile wastewater samples were used to ensure the field applicability of the newly synthesized adsorbent **4** for the treatment of dye contaminated effluents. All results regarding the removal of the DB-38 azo dye from the aqueous environment prop up resin **4** as an effective adsorbent and it was found that resin **4** has high adsorption efficiency toward the DB-38 azo dye at a wide range of pH as compared to **1** and **2**.

© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University.

1. Introduction

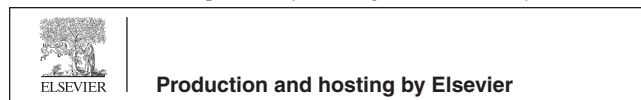
Since 1856, from the origin of synthetic dye to this day, a remarkable increase in the usage of synthetic dyes has been ob-

served. About 70% contribution of azo dyes in the total dye consumption makes them the representative and largest class of dyes used in textile-processing and other industries (Mustafa and Delia, 2004a,b). According to recent reports, due to easy, versatile and inexpensive synthesis in terms of cost effectiveness as well as high dyeing efficiency, approximately more than 10,000 different dyes and pigments are manufactured worldwide with a total annual production of over 7×10^5 metric tons per year (Saratale et al., 2011; Gnanamani et al., 2005; Chang et al., 2004; Devenci et al., 2004; Ghaedi et al., 2011a,b). Azo dyes are exclusively organic compounds consisting of a diazotized amine coupled to an amine or a phenol and contain one or more azo ($-N=N-$) linkages. Beside this, more than 500

* Corresponding author. Tel.: +92 (22) 9213430; fax: +92 (22) 9213431.

E-mail address: shahabuddinmemon@yahoo.com (S. Memon).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

azo dyes which are based on carcinogenic amines are also recognized as hazardous contaminants and must be removed from waste effluents prior to discharge (Bafana et al., 2008). Especially, due to the synthetic origin, recycling nature as well as complex aromatic structure, which helps them to resist their degradation; benzidine (BZ) based direct azo dyes are one of the problematic and bioresistant groups of organic pollutants (Golka et al., 2004; Ghaedi et al., 2011a,b).

On the basis of experimental studies with rats, dogs and epidemiological studies of workers exposed to the dyes, the National Institute for Occupational Safety and Health as well as the International Agency for Research on Cancer (IARC) have declared benzidine (BZ)-based dyes as carcinogenic and tumorigenic (Manning et al., 1985; Pinheiro et al., 2004; Ghaedi et al., 2012). However, in spite of the fact that, benzidine (BZ)-based azo dyes are health hazardous contaminants, they have been still in use in textile dyeing processes.

Since, benzidine based dyes are the inevitable source of environmental contamination, the removal of these dyes or in other words the decolorization of waste water is an imperative issue of the present era and extremely essential for environmental safety (Karagoz et al., 2011). Numerous researchers have taken considerable efforts to decontaminate the dye containing effluents 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 methodologies such as membrane filtration, coagulation/flocculation and adsorption (Saratale et al., 2011; Crini, 2006; Robinson et al., 2001).

Recent literature analysis reveals that among all the dye removal techniques the adsorption technique has proven to be an effective and attractive process for the decontamination of the dye-containing effluents. Consequently several researchers have adopted the adsorption approach to purify the industrial waste water by means of natural and synthetic adsorbents (Geethakarathi and Phanikumar, 2011; Chatterjee et al., 2010). The adsorption efficiency of the natural adsorbents varies from one material to another further more availability and their regeneration problems constrain their frequent use (Li et al., 2009).

Synthetic adsorbents such as calix[n]arene based silica resins due to their easy synthesis and regeneration may be a good choice of adsorbents for the decontamination of industrial effluent (Kamboh et al., 2011a,b; Chen et al., 2010). The dye remediation/decolorization of industrial effluent was based on the interaction between the surfaces of adsorbent and the adsorbed (polluted) species through the chemical bonding, hydrogen bonding, hydrophobic bonding and van der Waals forces (Parida et al., 2006). In this regard silica deserves particular attention, considering the chemical reactivity of its surface, due to the presence of silanol groups, which are weakly acidic and are very reactive. By virtue of the hydrophilic nature, the silica surface physically adsorbs water molecules. This property indicates that upon modification, the silica surface can be easily incorporated with the organic dye molecule in the aqueous environment. Furthermore, the chemical immobilization of calix[n]arene framework onto a polymeric backbone makes such a macrocycle a versatile material that not only helps in the remediation of polluted sites but also provides thermal stability and regenerable nature to the system (Yilmaz et al., 2006; Andrzejewska et al., 2007; Legrand, 1998).

The objective of the present study is to evaluate the adsorption efficiency of newly synthesized material i.e., *p-tert*-butylcalix[6]arene based silica resin (4) toward the Direct black 38 azo dye. Moreover, the influence of dosage, pH of the solution and the effect of electrolyte on the adsorption capacity of resin 4 have also been examined.

2. Experimental

2.1. Reagents

The commercial textile Direct Black 38 (FW: 781.7 g/mol, λ_{max} : 520 nm) benzidine based azo dye Fig. 1 was obtained from a commercially available source and used as an adsorbate without any further purification. The waste water samples were collected from textile and dye manufacturing industries. The appropriate amount of (0.1 N) HCl and/or NaOH has been used to 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 PF₂₅₄). 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. 010M, England). IR spectra were recorded on a Thermo Nicolet 5700 FT-IR 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 (Shelton, CT06484, and USA) Lambda 35 UV-vis spectrophotometer.

The pH measurements were made with a 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 the batch study.

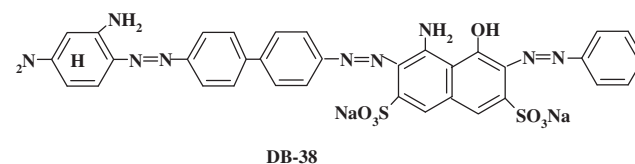


Figure 1 The chemical structures of adsorbate (DB-38 azo dye) used in experiments.

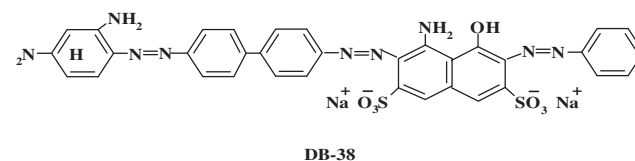


Figure 2 Structure of the DB-38 azo dye at higher (i.e. basic) pH.

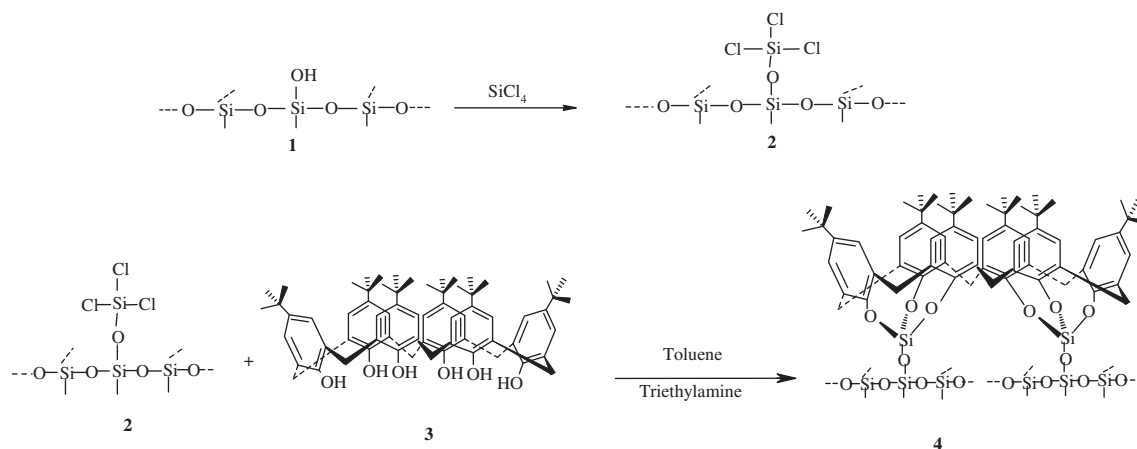


Figure 3 The synthesis of *p-tert*-butylcalix[6]arene based silica resin (4).

2.3. Synthesis

The modified silica (2) and *p-tert*-Butylcalix[6]arene (3) as illustrated in Fig. 3 were synthesized according to the previously published method (Gutsche et al., 1981; Katz et al., 2002).

2.3.1. Immobilization of *p-tert*-butylcalix[6]arene (3) onto the modified silica (2)

The immobilization of *p-tert*-butylcalix[6]arene (3) onto the surface of modified silica (2) was achieved by using 10 g of modified silica. A solution of 2 (2.97 g, 3.06 mmol) in chloroform (100 mL) was added to the modified silica 2 followed by the addition of triethylamine (15 g, 20.7 mL) and the reaction mixture was refluxed for a period of 50 h. The immobilization was monitored by FT-IR spectroscopy. The resulting grayish resin was filtered off, washed with excess of hot chloroform, methanol, water, and methanol respectively. Finally resin 4 was washed with hot chloroform (100 mL) and the resulting resin was dried at 100 °C under vacuum. The immobilization was confirmed by evaluating the FT-IR spectrum, SEM analysis and Thermogravimetric analysis (TGA) of 4.

2.4. Adsorption procedure for the DB-38 azo dye

2.4.1. Batch method

The adsorption capacity of resin 4 for the DB-38 Benzidine (BZ)-based direct azo dye from aqueous media was determined by batch wise tests. The experiments were conducted in 25 mL Erlenmeyer flasks with glass caps which contain particular amounts of the adsorbents as well as particular concentration of adsorbed solution. To obtain adsorption equilibrium, the Erlenmeyer flasks were stirred on a horizontal shaker operating at a constant speed (170 rpm) at 25 °C for a fixed time. The adsorbent was filtered and the adsorbed dye was analyzed by the UV-visible spectrophotometer. The % adsorption of azo dyes was calculated using Eq. (1) as follows:

$$\% \text{Adsorption} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i (mol L^{-1}) is the initial concentration of solution before sorption and C_f (mol L^{-1}) is the final concentration after the sorption of azo dye.

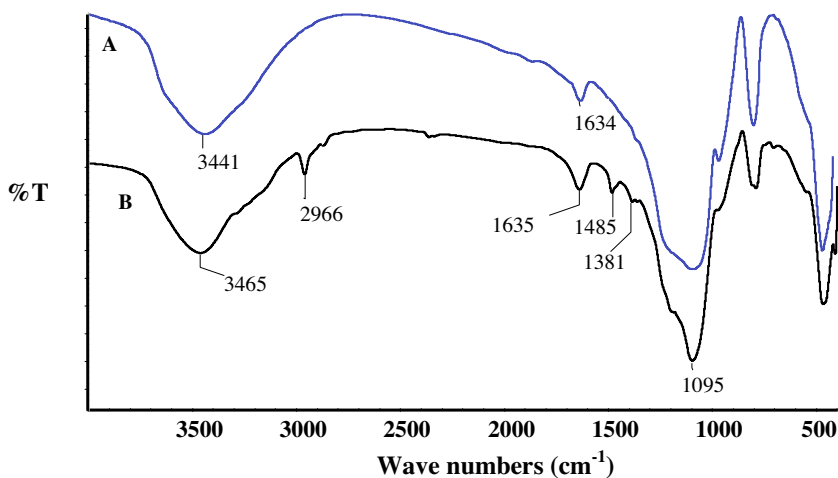


Figure 4 FT-IR spectra (A) pure silica (1) (B) resin 4.

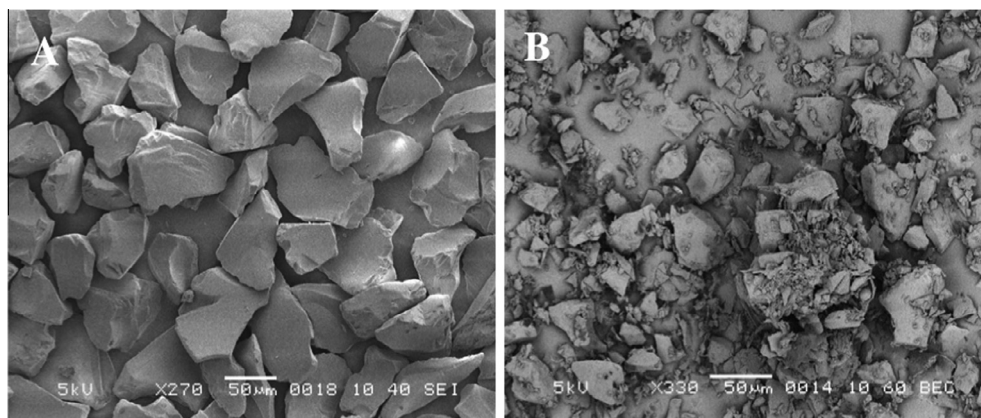


Figure 5 SEM images of (A) pure silica 1 (B) resin 4.

3. Results and discussion

3.1. Characterization

3.1.1. FT-IR spectra

Fig. 4 shows the FT-IR spectrum of pure silica (1) and resin 4. The spectrum of 1 is characterized by the strong absorbance at 1099 cm^{-1} which is the characteristic peak of asymmetric Si–O–Si stretching. The other characteristic peaks at 3441 cm^{-1} and 1632 cm^{-1} are due to O–H stretching and O–H bending respectively (Parida et al., 2006). While FT-IR spectral analysis of pure *p*-tert-butylcalix[6]arene shows clearly different bands at around 3340 cm^{-1} (OH), 2950 cm^{-1} (CH), 1500 cm^{-1} (C=C), 1340 cm^{-1} , (C–O) groups respectively (Gutsche et al., 1981). Consequently, following immobilization resin 4 shows some additional bands at 2966 , 1485 and 1381 cm^{-1} for –C–H, C=C and C–O groups of calixarene moiety (Fig. 3B) in FT-IR spectrum, which confirms the immobilization of *p*-tert-butylcalix[6]arene (3) onto the 2.

3.1.2. Scanning electron microscope (SEM)

Since, the sorption is a surface phenomenon, the rate and degree of sorption is highly dependent on the surface functional groups, pore size and surface area of the sorbent. Therefore,

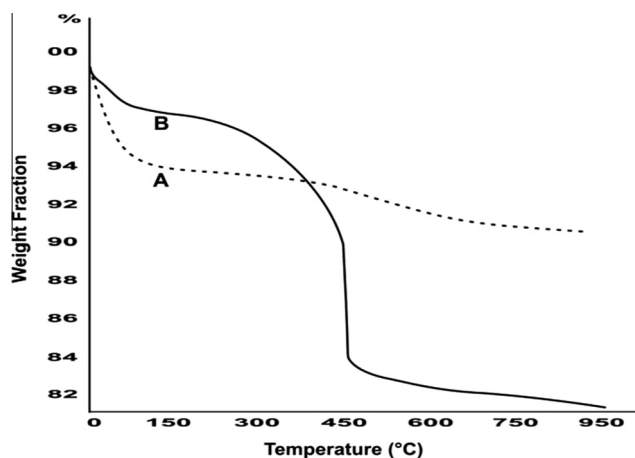


Figure 6 A & B. TGA curves pure silica 1 (A) resin 4 (B).

SEM is known as one of the most widely used surface diagnostic tools (Memon et al., 2008), for that reason SEM micrographs were obtained (by applying 05 kV electron acceleration voltage) to observe the surface morphology of pure silica (1) and material 4. The SEM images as shown in (Fig. 5A and B) are very demonstrative. Smooth morphology of silica (1) can be seen in Fig. 5A, following the immobilization of 3, as expected the smooth surface of silica 1 shows an irregular morphology (Fig. 5B) covered by a foreign material, i.e. 3. The coverage of smooth surface of silica 1 is with the foreign material which is presumably *p*-tert-butylcalix[6]arene aggregate. The coverage of silica surface as well as the presence of attached particles i.e., *p*-tert-butylcalix[6]arene (3) onto the surface of silica confirms the immobilization.

3.1.3. Thermogravimetric analysis (TGA)

Thermal stability of the *p*-tert-butylcalix[6]arene base silica resin (4) was examined by the TGA analyses, as presented in Fig. 6A and B. Two main steps on thermal degradation curves for pure silica (1) and *p*-tert-butylcalix[6]arene based silica resin (4) are observed as shown in Fig. 6A and B. The first step (Fig. 6B) ranging from (30 to $130\text{ }^{\circ}\text{C}$) was assigned to the loss

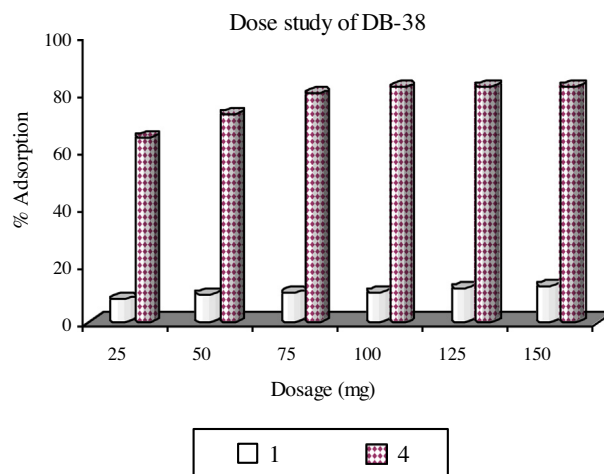


Figure 7 Effect of adsorbent dosage (1 and/or 4) on the percent adsorption of the DB-38 (Contact time 30 min, NaCl 0.3 M and dye concentration $2 \times 10^{-5}\text{ M}$).

of physically adsorbed water. The second step ranging from (250 to 450 °C) was recognized to the combustion of *p*-*tert*-butylcalix[6]arene (**3**) ring.

3.2. Adsorption study of selected the DB-38 azo dye

3.2.1. Effect of adsorbent dosage

To analyze the effect of adsorbent dosage (**1** and **4**) on the % adsorption of the DB-38 azo dye, the experiments were carried out by varying the amounts of adsorbent from 25 to 150 mg of **1** and **4** fixed dyes concentration (2×10^{-5} M). Fig. 7 obviously demonstrates that the % adsorption of the DB-38 azo dye slightly increased with increasing the dosage of adsorbents. The maximum dye removal efficiency has been achieved at 75 mg of the adsorbents, after which an increase in adsorbents dosage does not further improve the % adsorption and the dye removal efficiency remains almost constant. Thus, all the experiments were carried out with a fixed amount of adsorbents, i.e. 75 mg.

3.2.2. pH effect on the adsorption of azo dyes

It is well known that pH is most important and one of the main variable affecting factors during the dye adsorption process influencing not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry (Errais et al., 2011; Senturk et al., 2009). Fig. 8 shows the influence of the initial solution pH on the percent adsorption of the DB-38 dye onto resin **4**. The results (Fig. 8) revealed that the significant adsorption of the DB-38 azo dye occurs in a wide range of pH from pH 3 to pH 11. From Fig. 7, it has been noticed that the adsorption of the DB-38 dye increased with pH, while the value of pH changed from 3 to 9 and attains the maximum adsorption of 91% at pH 9.0. The adsorption of the DB-38 dye was decreased when the pH increased from 9 to 11.

The pH effect on the adsorption of the DB-38 dye observed in this study may be explained by the electrostatic interaction as well as metal ion coordination between resin **4** and the dye molecule. By increasing the pH of the system the number of negatively charged sites increases as well and the number of

positively charged sites decreases. Since, the DB-38 dye bore a sulfonate group, and in a basic environment as a result of the dissociation of sulfonate groups as represented in Fig. 2, the DB-38 dye became negatively charged and interacted with sodium ions as Fig. 9 describes it. In the same way, at a higher pH adsorbent i.e., *p*-*tert*-butylcalix[6]arene based silica resin (**4**) also becomes negatively charged and resin **4** becomes anionic in nature. In this scenario, a favorable environment was provided to the negatively charged resin **4** for electrostatic interactions with metal ions of the adsorbate; this facilitated adsorption. Moreover, negatively charged sites of *p*-*tert*-butylcalix[6]arene based silica resin (**4**) had the capability to bind sodium ions, and this implied an anion-pair extraction mechanism in which Na^+ coordinated with the negatively charged resin **4**, i.e. anionic sites of *p*-*tert*-butylcalix[6]arene based silica resin (**4**) along with the dye anions, and the rest of the dye molecules inserted themselves into the hydrophobic calixarene cavity (Fig. 9). In contrast, at a higher pH, the lower adsorption was attributed to the increase in the concentration of OH^- ions, which competed with the negative outer sites of the adsorbent. The electrostatic repulsions may suppress the dye adsorption but metal cation coordinated by negative sites of *p*-*tert*-butylcalix[6]arene based silica resin (**4**) and dye may eventually enhance the adsorption percentage. (Chen et al., 2010; Sidiras et al., 2011; Kamboh et al., 2011a,b).

3.2.3. Influence of the NaCl concentration on the adsorption of the DB-38 azo dye

Dye adsorption strongly depends on the ionic strength because the influence of electrolyte plays a key role on separation sciences. Thus, to recognize the electrolyte effect on adsorption of the DB-38 azo dye onto a newly synthesized adsorbent (i.e. resin **4**) the concentration of NaCl was varied from 0 to 0.5 mol L^{-1} . Fig. 10 represents the results obtained at different electrolytic concentrations, the results clearly point out that electrolytic concentration might be the important driving force in the DB-38 azo dye adsorption facilitated transport to the organic phase (Crini, 2003).

Fig. 10 deduced that dye adsorption increased with an increase of NaCl concentration up to 0.3 mol L^{-1} , above which there was no additional effect. This is due to the fact that NaCl

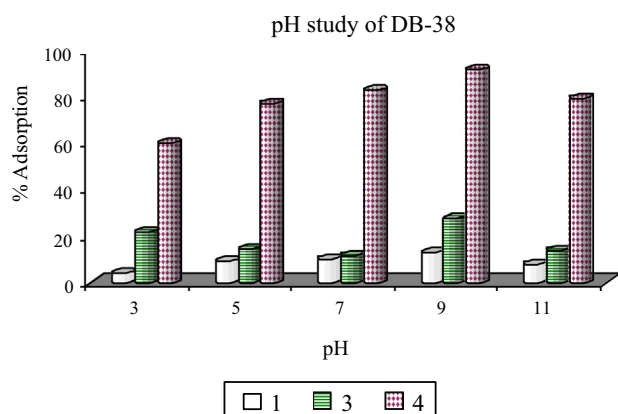


Figure 8 pH effect on the percent adsorption of the DB-38 azo dye. (Adsorbent dose 75 mg, Contact time 30 min, NaCl 0.3 M and dye concentration 2×10^{-5} M).

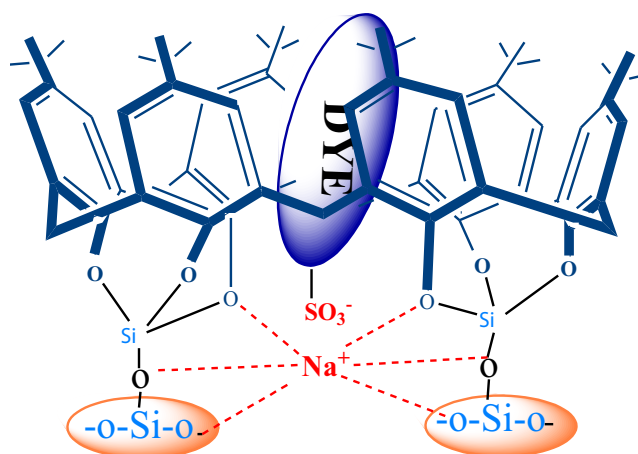


Figure 9 Proposed structure of interaction of the DB-38 azo dye with resin **4**.

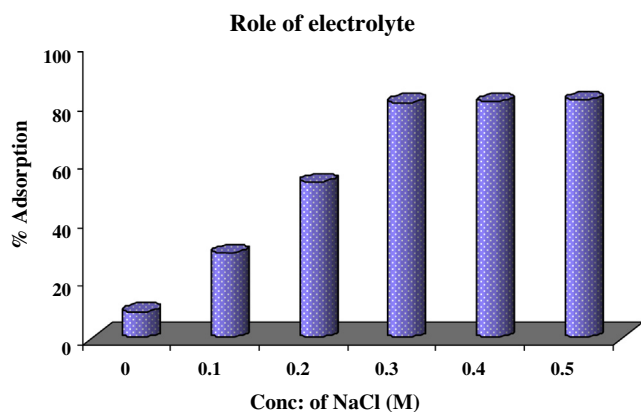


Figure 10 Effect of NaCl concentration on percent adsorption of the DB-38 (Adsorbent dose 75 mg, Contact time 30 min, dye concentration 2×10^{-5} M).

provides an ionic balance between the two phases and NaCl increases the solubility of the DB-38 azo dye through the common ion effect, resulting in an increase.

3.3. Regeneration of resin 4

Regeneration of resin 4 can easily be done by washing the solid material with an acid solution. The efficiency of resin 4 for the removal of the DB-38 azo dye decreases slightly with each cycle. The percent recovery of dyes was found to be 75–80%.

3.4. Field application of resin 4

The economic removal of the polluting dyes is an important problem. Therefore in order to authenticate the efficiency of the newly synthesized resin 4 as an effective adsorbent for the removal of the DB-38 dye from textile effluents, the decolorization of textile effluents containing the DB-38 as well as a mixture of different dyes and other auxiliary chemicals was also carried out. The batch study has been performed by using 75 mg adsorbent (resin 4) and 10 mL of dye waste water sample that has been stirred for 30 min, at 25 °C in 25 mL Erlenmeyer flasks. The concentration of the DB-38 was examined before and after the treatment of waste water with material 4. The field studies showed that material 4 reduces the concentration of the DB-38 azo dye 3.01×10^{-5} and 2.18×10^{-5} from 1.14×10^{-4} , and 9.13×10^{-5} for the samples 1 and 2, respectively. However up to 70% decolorization of real textile waste water samples corroborated 4 as a highly effective adsorbent for the treatment of industrial effluents contaminated with dyes.

4. Conclusions

New adsorbent, *p*-tert-butyl-calix[6]arene based silica resin (4), was synthesized successfully, FT-IR spectroscopy, scanning electron microscope (SEM) and thermo gravimetric analysis (TGA) confirmed the synthesis of resin 4. The adsorption of the Direct black-38 azo dye onto resin 4 has been investigated. The experimental results indicated that resin 4 is an effective

adsorbent for the removal of the DB-38 azo dye from the aqueous environment at a wide range of pH and the maximum adsorption of 91% was achieved at pH 9.0. For treatment of textile effluents, resin 4 presented extremely good performances and more than 70% decolorization has been achieved.

Acknowledgement

The authors thank the National Centre of Excellence in Analytical Chemistry, University of Sindh, Jamshoro, Pakistan, for the financial support of this work.

References

- Andrzejewska, A., Krysztafkiwicz, A., Jesionowski, T., 2007. Treatment of textile dye wastewater using modified silica. *Dyes Pigments* 75, 116–124.
- Bafana, A., Krishnamurthi, K., Devi, S.S., Chakrabarti, T., 2008. Biological decolorization of C.I. Direct Black 38 by *E. gallinarum*. *J. Hazard. Mater.* 157, 187–193.
- Chang, J.S., Chen, B.Y., Lin, Y.S., 2004. Stimulation of bacterial decolorization of an azo dye by extracellular metabolites from *Escherichia coli* strain NO3. *Bioresour. Technol.* 91, 243–248.
- Chatterjee, D., R.Patnam, V., Sikdar, A., Moulik, S.K., 2010. Removal of some common textile dyes from aqueous solution using fly ash. *J. Chem. Eng. Data* 55, 5653–5657.
- Chen, M., Chen, Y., Diao, G., 2010. Adsorption kinetics and thermodynamics of methylene blue onto *p*-tert-Butyl-calix[4,6,8]-arene-bonded silica gel. *Chem. Eng. Data* 55, 5109–5116.
- Crini, G., 2003. Studies on adsorption of dyes beta-cyclodextrin polymer. *Bioresour. Technol.* 90, 193–198.
- Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal. *Bioresour. Technol.* 97, 1061–1085.
- Deveci, T., Unyayar, A., Mazmanci, M.A., 2004. Production of remazol brilliant blue R decolourising oxygenase from the culture filtrate of *Funalia trogii* ATCC 200800. *J. Mol. Catal. B: Enzymatic* 30, 25–32.
- Errais, E., Duplay, J., Darragi, F., Rabet, I., Aubert, A., Huber, F., Morvan, G., 2011. Efficient anionic dye adsorption on natural untreated clay: kinetic study and thermodynamic parameters. *Desalination* 275, 74–81.
- Geethakarthis, A., Phanikumar, B.R., 2011. Industrial sludge based adsorbents/ industrial byproducts in the removal of reactive dyes, a review. *Int. J. Water Resour. Environ. Eng.* 3, 1–9.
- Ghaedi, M., Hossainian, H., Montazerzohori, M., Shokrollahi, A., Shojai pour, F., Soylak, M., Purkait, M.K., 2011a. A novel acorn based adsorbent for the removal of brilliant green. *Desalination* 281, 226–233.
- Ghaedi, M., Shokrollahi, A., Tavallali, H., Shojai poor, F., Keshavarzi, B., Hossainian, H., Soylak, M., Purkait, M.K., 2011b. Activated carbon and multiwalled carbon nanotubes an efficient adsorbents for kinetic and equilibrium study of removal of arsenazo (<IOTA> <IOTA> <IOTA>) and Methyl red dyes from waste water. *Toxicol. Environ. Chem.* 93, 438–449.
- Ghaedi, M., Najibi, A., Hossainian, H., Shokrollahi, A., Soylak, M., 2012. Kinetic and equilibrium study of alizarin red S removal by activated carbon. *Toxicol. Environ. Chem.* 94, 40–48.
- Gnanamani, A., Bhaskar, M., Ganeshjeevan, R., Chandrasekar, R., Sekaran, G., Sadulla, S., Ganga, R., 2005. Enzymatic and chemical catalysis of xyldine ponceau 2R and evaluation of products released. *Process Biochem.* 40, 3497–3504.
- Golka, K., Kopps, S., Myslak, Z.W., 2004. Carcinogenicity of azo colorants: influence of solubility and bioavailability. *Toxicol. Lett.* 151, 203–210.

- Gutsche, C.D., Dhawn, B., No, K.H., Muthukrishnan, R., 1981. Calixarenes. 4. The synthesis, characterization, and properties of the calixarenes from *p*-tert-butylphenol. *J. Am. Chem. Soc.* 103, 3782–3792.
- Kamboh, M.A., Solangi, I.B., Sherazi, S.T.H., Memon, S., 2011a. A highly efficient calix[4]arene based resin for the removal of azo-dyes. *Desalination* 268, 83–89.
- Kamboh, M.A., Solangi, I.B., Sherazi, S.T.H., Memon, S., 2011b. Sorption of Congo red onto *p*-tert-butylcalix[4]arene based silica resin. *J. Iran Chem. Soc.* 8, 272–279.
- Karagoz, B., Bayramoglu, G., Altintas, B., Bicak, N., Arica, M.Y., 2011. Amine functional monodisperse microbeads via precipitation polymerization of N-vinyl formamide: immobilized laccase for benzidine based dyes degradation. *Bioresour. Technol.* 102, 6783–6790.
- Katz, A., Costa, P.D., Lam, A.C.P., Notestein, J.M., 2002. The first single-step immobilization of a calix-[4]-arene onto the surface of silica. *Chem. Mater.* 14, 3364–3368.
- Legrand, A.P., 1998. *The Surface Properties of Silicas*. Wiley, New York.
- Li, Y., Gao, B., Wub, T., Wanga, B., Li, X., 2009. Adsorption properties of aluminum magnesium mixed hydroxide for the model anionic dye Reactive Brilliant Red K-2BP. *J. Hazard. Mater.* 164, 1098–1104.
- Manning, B.W., Cerniglia, C.E., Federle, T.W., 1985. Metabolism of the benzidine based azo dye DB 38 by human intestinal microbiota. *Appl. Environ. Microbiol.* 50, 10–15.
- Memon, G.Z., Bhangar, M.I., Akhtar, M., Talpur, F.N., Memon, J.R., 2008. Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent. *Chem. Eng. J.* 138, 616–621.
- Mustafa, I., Delia, S.T., 2004a. Decolorization and inhibition kinetic of Direct Black 38 azodye with granulated anaerobic sludge. *Enzymol. Microb. Technol.* 34, 147–158.
- Mustafa, I., Delia, S.T., 2004b. 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, 29–39.
- Parida, S.K., Dash, S., Patel, S., Mishra, B.K., 2006. Adsorption of organic molecules on silica surface. *Coll. Int. Sci.* 121, 77–110.
- Pinheiro, H.M., Touraud, E., Thomas, O., 2004. Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewaters. *Dyes Pigments* 61, 121–139.
- Robinson, T., McMullan, G., Marchant, R., Nigam, P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresour. Technol.* 77, 247–255.
- Saratale, R.G., Saratale, G.D., Chang, J.S., Govindwar, S.P., 2011. Bacterial decolorization and degradation of azo dyes: a review. *J. Taiwan Inst. Chem. Eng.* 42, 138–157.
- Senturk, H.B., Ozdes, D., Gundogdu, A., Duran, C.M., 2009. Removal of phenol from aqueous solutions by adsorption onto organomodified tirebolu bentonite: equilibrium, kinetic and thermodynamic study. *J. Hazard. Mater.* 172, 353–362.
- Sidiras, D., Batzias, F., Schroeder, E., Ranjan, R., Tsapatsis, M., 2011. Dye adsorption on autohydrolyzed pine sawdust in batch and fixed-bed systems. *Chem. Eng. J.* 171, 883–896.
- Yilmaz, M., Memon, S., Tabakci, M., Bartsch, R.A., 2006. New frontiers in polymer research. In: Bregg, R.K. (Ed.). Nova publishers, New York, pp. 25–172.