



# Synthesis and application of calix[4]arene based resin for the removal of azo dyes

Muhammad Afzal Kamboh, Imam Bakhsh Solangi, S.T.H. Sherazi, Shahabuddin Memon\*

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

## ARTICLE INFO

### Article history:

Received 19 May 2009

Received in revised form 30 June 2009

Accepted 30 June 2009

Available online 5 July 2009

### Keywords:

Calixarene

Immobilization

Amberlite resin

Azo dye

Solid-phase extraction

Batch-wise sorption

## ABSTRACT

The present study describes a novel synthetic method for the immobilization of calix[4]arene (**II**) onto the surface of modified Amberlite XAD-4 resin (**4**), which does not require the derivatization of calixarene moiety. The novel calix[4]arene based resin (C4 resin) **5** was used as sorbent for the removal of azo dyes. Batch-wise sorption study was carried out and observed that the C4 resin (**5**) is more effective as compared to compound **II** as well as pure Amberlite XAD-4 resin (**1**) to remove the selected dyes [i.e. Reactive Black-5 (RB-5), Reactive Red-45 (RR-45) and Congo Red (CR)]. The effect of sorbent dosage and pH on % sorption was studied. During the extraction process, various kinds of interactions such as electrostatic repulsion, deprotonation of the hydroxyl groups of C4 resin, dissociation of reactive dyes into anions/cations and structural variations were monitored and found that they are highly pH dependent.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Azo dyes are very important class of synthetic chemicals [1] known as organic colorants commonly prepared by coupling of a diazonium compound with a phenol or an aromatic amine [2]. Approximately half of all known colorants are azo dyes [3] and having extensive application in various fields, such as textile and fibers, pulp and paper, dyeing, paint, laser, liquid crystalline displays, ink-jet printer and electro-optical devices. [4]. Although some azo dyes are toxic in nature, these dye molecules are biologically inactive, but the living organisms are able to cleave the azo (N=N) groups [5–7], forming aromatic amines most of them are also toxic and even carcinogenic [8] which affect the human health by direct contact or through the environment [9]. Toxic effects of the dye intermediates, i.e., aromatic amines on the human health have been reported [10]. Platzek et al. reported the absorption of aromatic amines *via* skin by skin bacteria [11]. The presence of aromatic amines in the urine samples of the dyestuff workers has also been reported [12,13] and the influence of azo dyes causes cancer in human bladder [14]. The exposure of azo dyes in the environment due to loss of dyes during the dyeing process by many industries causes the major environmental problems [15,16]. The worldwide consumptions of total dyes are in excess of  $10^7$  kg per year [17]. These industries release 10–15% of the dye during the dyeing process and approximately one million kilograms per year of dyes are discharged into water streams con-

taining different types of un-reacted dyes which are mostly health hazardous [18–20]. Due to the toxicity of these dyes and their intermediates the European Parliament has recently approved the ban in 19th amendment for the use of twenty two aromatic amines [21].

Hence, the removal of color from waste effluents has significant importance to the environment [22,23]. Conventional biological treatments and physicochemical methods are not sufficient to remove the azo dyes from effluent because of their stability, fastness and higher solubility in water [24–26]. Generally, following methods are applied for the treatment of dye-containing effluent: coagulation–flocculation, membrane processes [27], oxidation–ozonation [28], biological treatment and sorption [29]. Among these, sorption process is one of the most efficient methods for the removal of dye molecules from wastewater, because it provides a simple, fast, cost-effective and reusable process [30]. Activated carbon, peat, chitin, silica, fly ash, clay and others were used as sorbents, but the sorption capacity of these sorbents is not effective. Therefore, to enhance the sorption performance new sorbents are still under investigation [31].

However synthetic macromolecular compounds such as calixarenes are extensively being employed as trapping agents for ionic as well as neutral species. Immobilization of supramolecule, i.e., cyclodextrin and/or calix[*n*]arene framework onto a particular resin makes such macrocycle not only selective for the detection due to its chromogenic behavior but also helps in the remediation of industrial organic molecules such as azo dyes [32–35]. Thus, Amberlite XAD resins have received a considerable attention as basic matrixes for designing new chelating resins [36,37]. These resins possess enormous advantages over the others; for example, structure of these resins provides excellent chemical, physical and

\* Corresponding author. Tel.: +92 22 2772065; fax: +92 22 2771560.

E-mail addresses: [memons@ceacsu.edu.pk](mailto:memons@ceacsu.edu.pk), [shahabuddinmemon@yahoo.com](mailto:shahabuddinmemon@yahoo.com) (S. Memon).

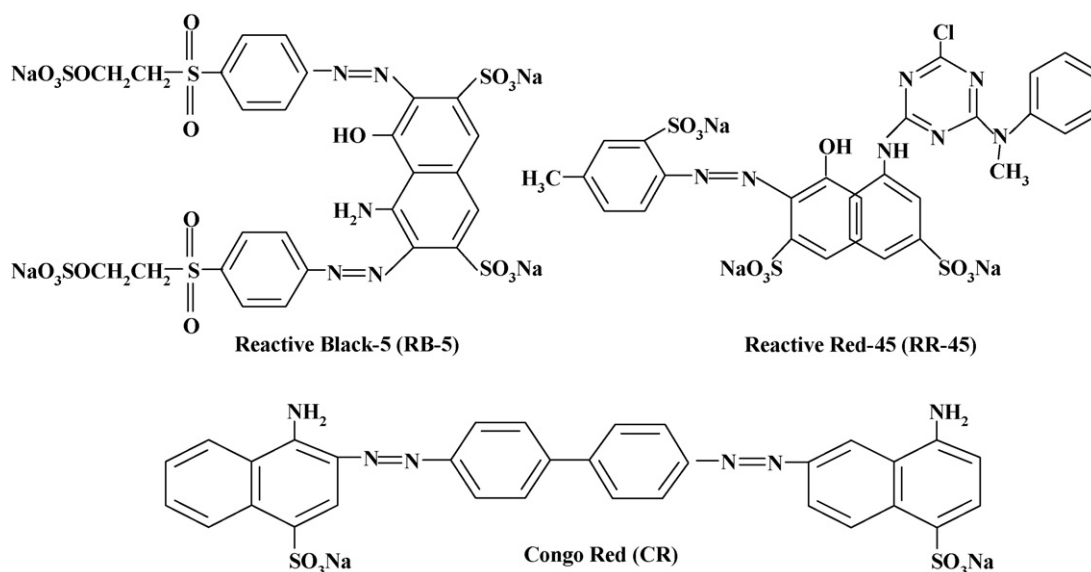


Fig. 1. The chemical structures of some selected azo dyes used in experiments.

thermal stability under various experimental conditions. Moreover, chelating agents can be easily immobilized onto their surfaces with high stability [38,39]. Amberlite XAD-4 is a co-polymeric sorbent which is highly stable at all pH range in aqueous solution and its pore size distribution makes it an excellent sorbent for organic substances of relatively low molecular weight [40]. The main focus of this study was to enhance the sorption property of the Amberlite XAD-4 resin (**1**) by immobilizing calix[4]arene (**II**) onto its surface. Furthermore, the influence of dose and pH of the solution on the sorption capacity of modified (C4) resin (**5**) has also been examined.

## 2. Experimental

### 2.1. Apparatus

Melting points were determined on a Gallenkamp melting-point apparatus model MFB.595.010M, England. IR spectra were recorded on a Thermo Nicolet 5700 FT-IR spectrometer (WI. 53711, USA) as KBr pellets. Elemental analyses were performed using a CHNS instrument model Flash EA 1112 elemental analyzer (20090; Rodano, Milan, Italy). Scanning electron microscopic studies were performed using JSM-6380 instrument. UV–vis spectra were recorded on a Perkin Elmer (Shelton, CT 06484, USA) Lambda 35 through 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.

### 2.2. Reagents

Analytical grade reagents/chemicals were used for the preparation of all the solutions. Analytical TLC was performed on pre-coated silica gel plates ( $\text{SiO}_2$ , Merck PF<sub>254</sub>). NaOH, formaldehyde, diphenyl ether, acetone, acetic acid, ethanol (all Merck) were used as received. The pHs 3–11 were prepared by mixing appropriate amount of 0.1 M (HCl/KOH). Azo dyes such as Reactive Black-5 (RB-5), Reactive Red-45 (RR-45) and Congo Red (CR) obtained from commercially available source were used in this study (Fig. 1).

Amberlite XAD-4 (surface area of  $750 \text{ m}^2 \text{ g}^{-1}$ , pore diameter 1–3 nm and bead size 20–50 mesh) was procured from Fluka (Germany). The surface area, pore diameter and mesh size were quoted by the supplier. The resin was washed with distilled water and ethanol before use. All aqueous solutions were prepared with deionized water that had been passed through a Milli-Q system (Elga Model Classic UVF, UK).

### 2.3. Synthesis

*p*-tert-Butylcalix[4]arene (**I**) and calix[4]arene (**II**) as illustrated in Fig. 2 were synthesized according to the previously published methods [41,42].

#### 2.3.1. Immobilization of calix[4]arene (**II**) onto Amberlite XAD-4 resin (**4**)

Amberlite XAD-4<sup>TM</sup> has been modified as shown in Fig. 3 (2–4) according to the previously reported method [43]. Finally, the immobilization of (**II**) onto (**4**) was carried out as follows.

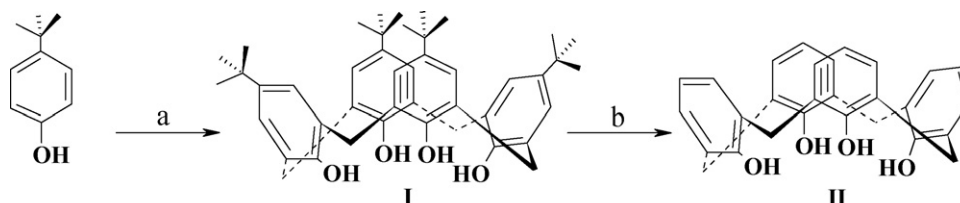


Fig. 2. Synthesis of calix[4]arene (**II**): (a)  $\text{HCHO}/\text{OH}^-$  and (b)  $\text{AlCl}_3$ -phenol/toluene.

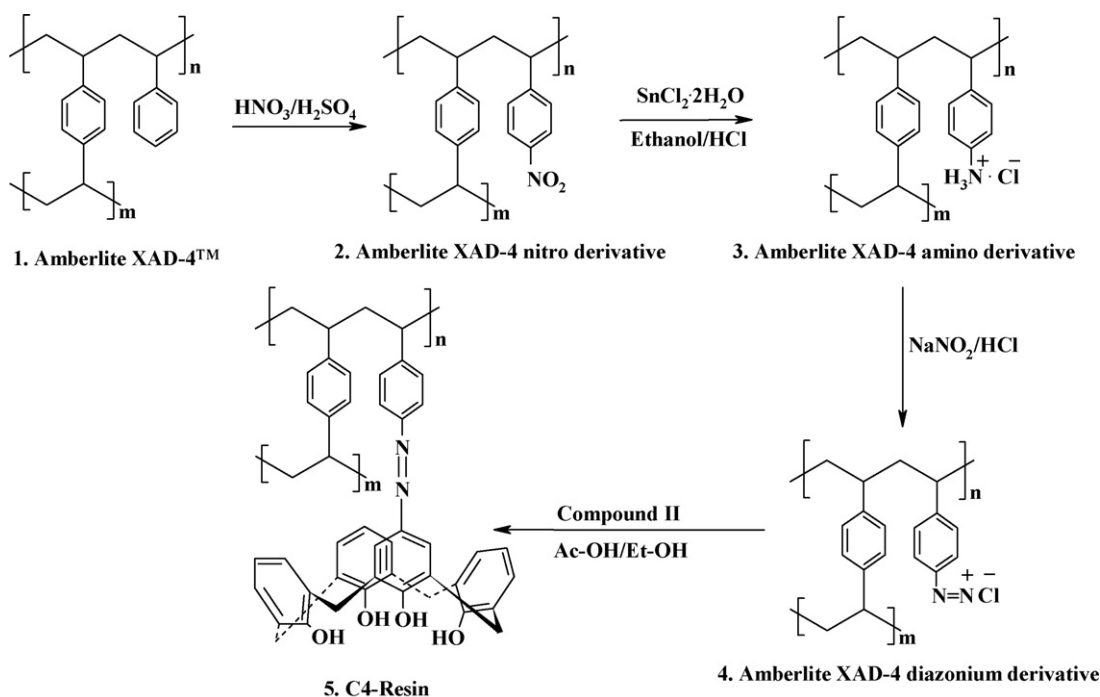


Fig. 3. Immobilization of calix[4]arene (II) onto the modified Amberlite XAD-4 resin 4.

The diazotized resin **4** (5 g) was reacted with calix[4]arene **II** (5 mmol, 2.12 g) in 400 mL of glacial acetic acid and acetone (3:1) at 0–3 °C for 24 h. The resulting grayish colored beads were filtered off, washed with distilled water and chloroform and then air-dried. At last, the immobilization was confirmed by evaluating FT-IR spectrum of C4 resin **5**, SEM and elemental analysis. Found: C, 76.93; H, 6.55; N, 3.72%. Calculated for  $C_{46}H_{41}N_2O_4 \cdot 2H_2O$ : C, 76.54; H, 6.28; N, 3.88%.

The structure shown in Fig. 3 does, however, have a polymeric structure with both  $m$  and  $n$  repeating units. From the elemental analysis results it has been found that the value for these both variables is approximately equal to 1, i.e.,  $m = n$ .

## 2.4. Sorption procedures

### 2.4.1. Batch method

Batch-wise sorption study was carried out for azo dyes at room temperature, i.e.,  $35 \pm 1$  °C. The azo dye sample solution 10 mL ( $2 \times 10^{-5}$  M) containing NaCl (0.2 M) was taken in a glass-stoppered bottle. To this solution the C4 resin (100 mg) was added and stirred on a horizontal shaker operating at a constant agitation speed of 170 rpm until equilibrium for 1 h. The resin was filtered and the sorbed dye was analyzed by UV–vis spectrophotometer. Absorbance values were recorded at  $\lambda_{max}$  for each azo dye solution at 597, 540 and 496 nm for RB-5, RR-45 and CR, respectively. The sorption of azo dyes was calculated as follows:

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

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

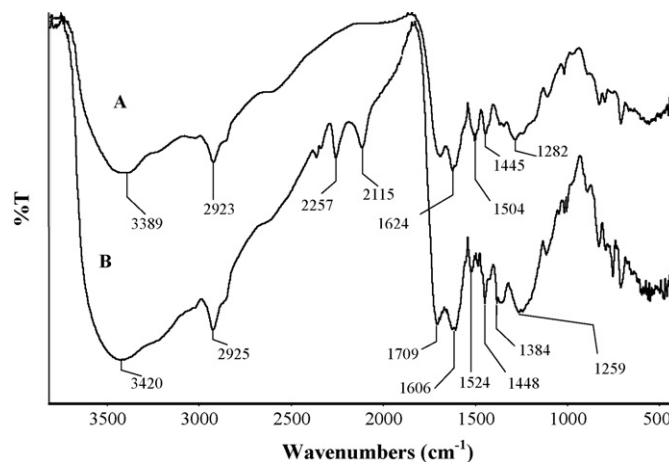


Fig. 4. FT-IR spectra: (A) Amberlite amino derivative 4 and (B) C4 resin 5.

## 3. Results and discussion

### 3.1. Characterization

#### 3.1.1. FT-IR spectra

The characterization of Amberlite XAD-4 resins (**1–4**) by FT-IR spectroscopy was reported [43] previously; while the newly synthesized C4 resin (**5**) shows some additional bands at 1384, 1448, 1709 and  $2115 \text{ cm}^{-1}$  for  $-\text{C}-\text{N}$  and  $\text{N}=\text{N}$  groups (Fig. 4), which confirms the immobilization of calix[4]arene onto the resin.

#### 3.1.2. Scanning electron microscope (SEM)

Since, the sorption is a surface phenomena, the rate and degree of sorption is specific for a given sorbent that is influenced by its physicochemical properties such as surface area, pore size, surface functional groups and composition. The morphological characteristics of C4 resin (**5**) were evaluated using a scanning electron

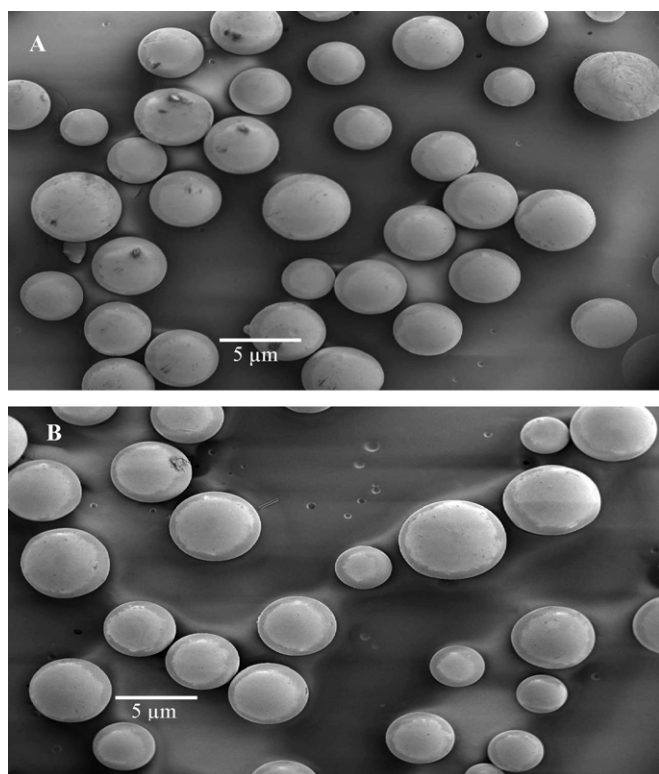


Fig. 5. SEM images of: (A) Amberlite XAD-4 1 and (B) C4 resin 5.

microscope (SEM) by applying 05 kV electron acceleration voltage. Fig. 5A shows the SEM micrographs of the pure Amberlite XAD-4 resin at 20 times magnification. It can be seen from the XAD-4 image showing the rough and porous surface [43]. After the immobilization of calix[4]arene onto Amberlite XAD-4 at 130 times magnification, the beads of immobilized resin (Fig. 5B) show very smooth and regular shapes covered by foreign material, i.e., calix[4]arene.

### 3.2. Sorption study of selected azo dyes

#### 3.2.1. Effect of sorbent dosage

The sorbent dosage is a major parameter because this concludes the capacity of a sorbent for given initial concentration of the sorbet at the operating conditions. The influence of the dosage of C4 resin and pure Amberlite resin on the sorption of azo dyes using contact time, i.e., 1 h is represented in Fig. 6A and B. The molar concentration of dyes was kept constant ( $2 \times 10^{-5}$  M), while quantity of C4 resin and pure Amberlite resin was varied between 25–100 mg. It was observed that the sorption of azo dyes increases by increasing the dosage of C4 resin as well as pure Amberlite resin. It has been observed that almost maximum sorption was achieved at 100 mg. This was because of the availability of more and more sorbent surface for the given concentration of azo dyes to be sorbed.

#### 3.2.2. Effect of pH on the sorption

The pH is an important parameter in sorption phenomena and plays a vital role in the entire sorption process and especially on the sorption capacity [44]. As in this study, to evaluate the influence of pH on the sorption of azo dyes onto the C4 resin, pure Amberlite resin and calix[4]arene ligand, experiments were carried out at different pH (i.e. 3.0, 5.0, 7.0, 9.0 and 11.0). The results obtained are shown in Fig. 7A and B.

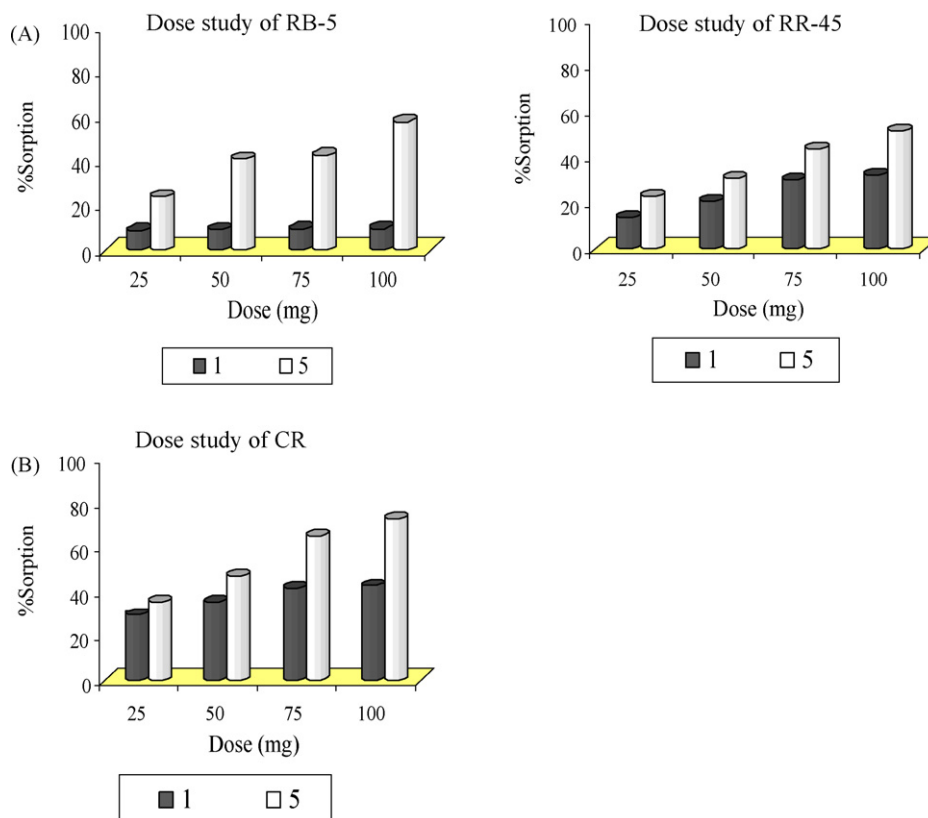
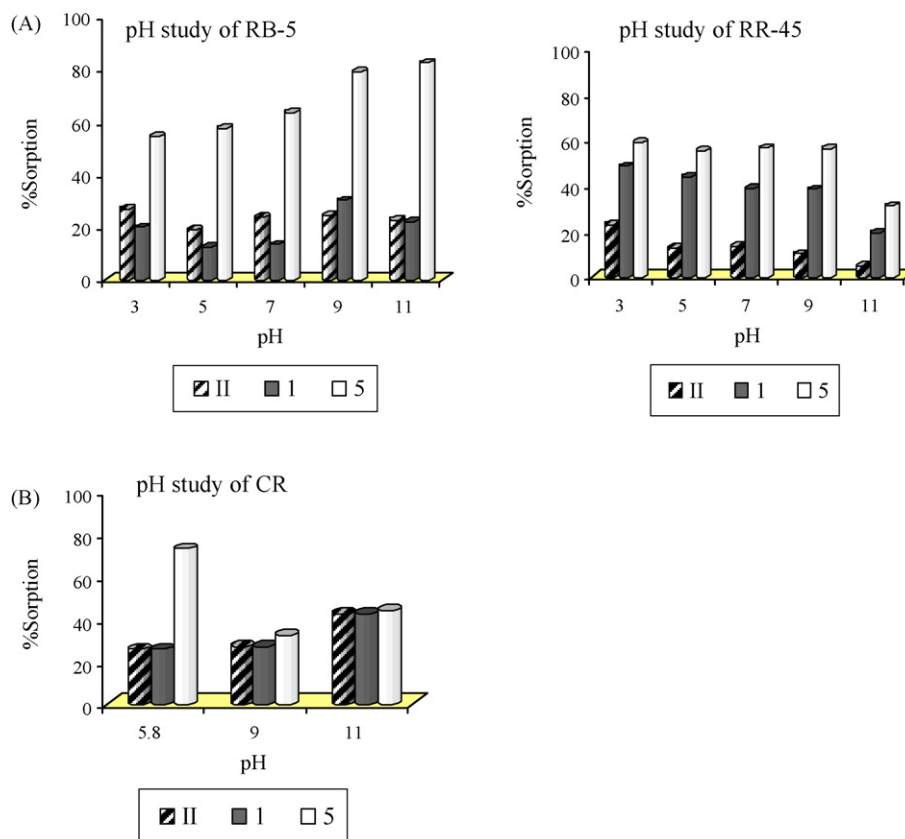


Fig. 6. (A) Effect of sorbent dosage (1 and 5) on the percent sorption of RB-5 and RR-45. (Contact time 1 h, NaCl 0.2 M dye concentration  $2 \times 10^{-5}$  M.) (B) Effect of sorbent dosage on the percent sorption of CR. (Contact time 1 h, dye concentration  $2 \times 10^{-5}$  M.)



**Fig. 7.** (A) pH effect on the percent sorption of RB-5 and RR-45 (sorbent dose 100 mg, contact time 1 h, NaCl 0.2 M dye concentration  $2 \times 10^{-5}$  M). (B) pH effect on the percent sorption of CR (sorbent dose 100 mg, contact time 1 h, dye concentration  $2 \times 10^{-5}$  M).

From the results (Fig. 7A and B) it has been deduced that the C4 resin (5) is more efficient than pure Amberlite resin (1) and calix[4]arene ligand (II). The percent sorption of RB-5 for C4 resin it attains a maximum value of 82% at pH 11. This is due to the fact that RB-5 is comparatively a large molecule and negatively charged at higher pH (i.e. pH 11). Upon dissolution, the ionic dyes liberate dye anions/cations into solution. Furthermore, in aqueous media sulfonate groups of acid dye after dissociation become negatively charged. Following the deprotonation of the phenolic hydroxyl groups of calix[4]arene moiety in C4 resin, also form negatively charged phenoxide ions at higher pH. In this situation by virtue of hydrophobic interaction and metal ion coordination the dyes are extracted. The deprotonation not only suppress the electrostatic repulsion between the dye and sorbent but also at the same time, it provides a favorable environment in which the metal cation of dye molecule coordinates with the negative sites of sorbent and improve the extraction percentage [35].

The pH of solution also plays a significant role for the sorption of CR, because the addition of electrolyte (NaCl) and pH affects the structural stability as well as its color intensity. In acidic conditions (pH range 2.0–5.5) CR changes its color from red to dark blue [45]. Due to the structural variations of CR molecule at lower pH, all the sorption experiments were performed at its original pH (i.e. 5.8) without electrolyte (NaCl) and at pH 9 as well as at pH 11. The results obtained show that the maximum sorption 72% of CR for C4 resin (5) was achieved at its original pH (i.e. 5.8) while by increasing the pH of dye solution percent sorption decreases. CR is a dipolar molecule, at acidic pH it exists as cationic form and at basic pH exists as anionic form. At higher pH, the phenolic (OH) functional group of C4 resin becomes phenoxide ( $\text{Ph-O}^-$ ) ion, which does not

favor the sorption of the dye anions due to the electrostatic repulsion between negatively charged sites on sorbent and dye anion. CR shows lower sorption at higher pH [46].

Effect of pH on sorption of RR-45 onto C4 resin (5) was studied at pH (3–11). The result obtained shows that by increasing the pH sorption decreases and it attains maximum value 60% at pH 3, while 52% at its original pH and 30% at pH 11. The main mechanism is anion exchange, the anionic dye must be in competition with ( $\text{OH}^-$ ) the phenolic hydroxyl groups of calix[4]arene moiety in C4 resin for exchange with the  $\text{Cl}^-$  ions that are associated with the surface of sorbent on the other hand, the sorbent surface becomes negatively charged due to deprotonation and will be associated with positively charged ions of the solution. Thus, a significant decrease in dye sorption occurred at pH greater than 9 [47].

#### 4. Conclusion

In this study a novel C4 resin (5) was synthesized and characterized by FT-IR spectroscopy, elemental analysis (CHNS) and scanning electron microscope (SEM) techniques. Newly synthesized C4 resin, calix[4]arene (II) and Amberlite XAD-4<sup>TM</sup> resin (1) have been used successfully as sorbents for the removal of RB-5, RR-45 and CR. The effects of dosages of sorbents and pH of dye solution were investigated in batch sorption experiments. The results achieved from the present study clearly show that C4 resin is a very efficient sorbent for the removal of selected dyes as compared to the calix[4]arene (II) and Amberlite XAD-4<sup>TM</sup> resin (1). It has been observed that % sorption is highly dependent on sorbent dosage, pH of dye solution and presence of functional groups attached to the dye molecule. On the basis of the results it can be concluded that:

- (1) The % sorption of dyes could be enhanced by immobilization of calix[4]arene (II) onto the surface of modified Amberlite XAD-4 resin.
- (2) The sorption of RR-45 and CR by C4 resin from aqueous solution must be carried out at their original pH, while the sorption of RB-5 must be studied at higher pH (i.e. pH 11).

### Acknowledgement

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

### References

- [1] R.A. Hoodles, K.G. Pitman, T.E. Stewart, J. Thompson, J.E. Arnold, Separation and identification of food colors. Identification of synthetic water soluble food colors using thin-layer chromatography, *J. Chromatogram* 54 (1971) 393–404.
- [2] K. Golka, S. Kopps, Z.W. Myslak, Carcinogenicity of azo colorants: influence of solubility and bioavailability, *Toxicol. Lett.* 151 (2004) 203–210.
- [3] T. Günseli, O. Mustafa, Preparation and characterization of chromophore group containing cyclotriphosphazenes: V. Spectroscopic investigation of some hexakis (*p*-phenylazo- $\alpha$ -naphthoxy) cyclotriphosphazenes, *Dyes Pigments* 70 (2006) 117–125.
- [4] 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, *Process Biochem.* 40 (2005) 3497–3504.
- [5] I.M. Banat, P. Nigam, G. McMullan, R. Marchant, The isolation of thermophilic bacterial culture capable of textile dyes decoloration, *Environ. Int.* 23 (1997) 547–551.
- [6] A. Stolz, Basic applied aspects in the microbial degradation of azo dyes, *Appl. Microbiol. Biotechnol.* 56 (2001) 69–80.
- [7] J.D. Spikes, R. Straight, Sensitized, Photochemical processes in biological systems, *Annu. Rev. Phys. Chem.* 18 (1967) 409–436.
- [8] K.T. Chung, Mutagenicity and carcinogenicity of aromatic amines metabolically produced from azo dyes, *Environ. Carcinogen Ecotoxicol. Rev.* C18 (2000) 51–71.
- [9] A. Plum, W. Engewald, A. Rehorek, Rapid qualitative pyrolysis GC–MS analysis of carcinogenic aromatic amines from dyed textiles, *Chromatographia* 57 (2003) 243–248.
- [10] A. Gnanamani, M. Bhaskar, R. Ganga, G. Sekaran, S. Sadulla, Chemical and enzymatic interactions of Direct Black 38 and Direct Brown 1 on release of carcinogenic amines, *Chemosphere* 56 (2004) 833–841.
- [11] T. Platzek, U.S. Gi, C. Lang, W. Baltes, Formation of a carcinogenic aromatic amine from an azo dye by human skin bacteria in vitro, *Hum. Exp. Toxicol.* 18 (1999) 552–559.
- [12] C.E. Cerniglia, J.P. Freeman, W. Franklin, L.D. Pack, Metabolism of benzidine and benzidine congeners based dyes by humans, monkey and rat intestinal bacteria, *Biochem. Biophys. Res. Commun.* 107 (1982) 1224–1229.
- [13] 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.
- [14] Z.A. Medvedev, H.M. Crowne, M.N. Medvedeva, Age related variations of hepatocarcinogenic effect of azo dye (30-MDAB) as linked to the level of hepatocyte ployploidization, *Mech. Ageing Dev.* 46 (1988) 159–174.
- [15] C.S. Eskilsson, R. Davidsson, L. Mathiasson, Harmful azo colorants in leather. Determination based on their cleavage and extraction of corresponding carcinogenic aromatic amines using modern extraction techniques, *J. Chromatography A* 955 (2002) 215–227.
- [16] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, The removal of color from textile waste water using whole bacterial cells: a review, *Dyes Pigments* 58 (2003) 179–196.
- [17] G.M. Shaul, T.J. Holdsworth, C.R. Dempsey, K.A. Dostall, Fate of water soluble azo dyes in the activated sludge process, *Chemosphere* 22 (1991) 107–119.
- [18] I.M. Bassat, P. Nigam, D. Singh, R. Marchant, Microbial decolorization of textile–dye-containing effluents: a review, *Bioresour. Technol.* 58 (1996) 217–227.
- [19] E.J. Weber, V.C. Stickney, Hydrolysis kinetics of reactive blue 19–vinyl sulfone, *Water Res.* 27 (1993) 63–67.
- [20] V. Kokol, A. Doliska, I. Eichlerova, P. Baldrian, F. Nerud, Decolorization of textile dyes by whole cultures of *Ischnoderma resinosa* and by purified laccase and Mn-peroxide, *Enzyme Microb. Technol.* 40 (2007) 1673–1677.
- [21] European Commission, Off. J. Eur. Commun. L243 (2002) 15.
- [22] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere* 50 (2003) 1095–1105.
- [23] M.S. Chiou, H.Y. Li, Equilibrium and kinetic modeling of adsorption reactive dye on cross-linked chitosan beads, *J. Hazard. Mater.* 93 (2002) 233–248.
- [24] D. Roy, K.T. Valsaraj, S.A. Kottai, Separation of organic dyes from wastewater by using colloidal gas aphanes, *Sep. Sci. Technol.* 27 (1992) 573–588.
- [25] M. Özacar, I.A. Sengil, Adsorption of reactive dyes on calcined alunite from aqueous solutions, *J. Hazard. Mater.* B98 (2003) 211–224.
- [26] J. Yener, T. Kopac, G. Dogu, T. Dogu, Dynamic analysis of sorption of Methylene Blue dye on granular and powdered activated carbon, *Chem. Eng. J.* 144 (2008) 400–406.
- [27] F. Harrelkas, A. Azizi, A. Yaacoubi, A. Benhammou, M.N. Pons, Treatment of textile dye effluents using coagulation–flocculation coupled with membrane processes or adsorption on powdered activated carbon, *Desalination* 235 (2009) 330–339.
- [28] V.P. Santos, M.F.R. Pereira, P.C.C. Faria, J.J.M. Orfao, Decolorisation of dye solutions by oxidation with H<sub>2</sub>O<sub>2</sub> in the presence of modified activated carbons, *J. Hazard. Mater.* 162 (2009) 736–742.
- [29] S.R. Couto, Dye removal by immobilised fungi, *Biotechnol. Adv.* 27 (2009) 227–235.
- [30] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, *Waste Manage.* 21 (2001) 381–387.
- [31] I. Uzun, Kinetics of the adsorption of reactive dyes by chitosan, *Dyes Pigments* 70 (2006) 76–83.
- [32] M. Yilmaz, S. Memon, M. Tabakci, R.A. Bartsch, Design of polymer appended calixarenes as ion carriers, in: R.K. Bregg (Ed.), *New Frontiers in Polymer Research*, Nova Publishers, New York, 2006, pp. 125–172.
- [33] S. Memon, M. Yilmaz, D.M. Roundhill, Remediation, Liquid–liquid phase transfer extraction of chromium(VI). A review, *Collect. Czech. Chem. Commun.* 69 (2004) 1231–1250.
- [34] E.Y. Ozmen, M. Yilmaz, Use of  $\beta$ -cyclodextrin and starch based polymers for sorption of Congo red from aqueous solutions, *J. Hazard. Mater.* 148 (2007) 303–310.
- [35] O. Gungor, S. Memon, A. Yilmaz, M. Yilmaz, Evaluation of the performance of calix[n]arene derivatives as liquid phase extraction material for the removal of azo dyes, *J. Hazard. Mater.* 158 (2008) 202–207.
- [36] V.K. Jain, S.S. Sait, P. Shrivastav, Y.K. Agrawal, Application of chelate forming resin Amberlite XAD-2-o-vanillinthiosemicarbazone to the separation and preconcentration of copper(II), zinc(II) and lead(II), *Talanta* 45 (1997) 397–404.
- [37] P.K. Tewari, A.K. Singh, Preconcentration of lead with Amberlite XAD-2 and Amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry, *Talanta* 56 (2002) 735–744.
- [38] N. Ozdemir, M. Soylak, L. Elci, M. Doganc, Speciation analysis of inorganic Sb(III) and Sb(V) ions by using mini column filled with Amberlite XAD-8 resin, *Anal. Chim. Acta* 50 (2004) 537–541.
- [39] V.A. Lemos, P.X. Baliza, Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper, *Talanta* 67 (2005) 564–570.
- [40] H. Rohm, Amberlite XAD-4, Preliminary Technical Notes, Amberlite XAD-7, Technical Notes, 1982.
- [41] C.D. Gutsche, M. Iqbal, D. Stewart, Synthesis procedures for P-tert-butyl calix[4]arene, *J. Org. Chem.* 51 (1986) 742–745.
- [42] C.D. Gutsche, L.-G. Lin, The synthesis of functionalized calixarenes, *Tetrahedron* 42 (1986) 1633–1640.
- [43] I.B. Solangi, S. Memon, M.I. Bhangar, Synthesis and application of a highly efficient tetraester calix[4]arene based resin for the removal of Pb<sup>2+</sup> from aqueous environment, *Anal. Chim. Acta* 638 (2009) 146–153.
- [44] G.Z. Memon, M.I. Bhangar, M. Akhtar, F.N. Talpur, J.R. Memon, Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent, *Chem. Eng. J.* 138 (2008) 616–621.
- [45] B. Acemioglu, Adsorption of Congo red from aqueous solution onto calcium-rich fly ash, *J. Colloid Interface Sci.* 274 (2004) 371–379.
- [46] M.K. Purkait, A. Maiti, S.D. Gupta, S. De, Removal of Congo red using activated carbon and its regeneration, *J. Hazard. Mater.* 145 (2007) 287–295.
- [47] Y. Li, B. Gao, T. Wub, B. Wang, X. Li, Adsorption properties of aluminum magnesium mixed hydroxide for the model anionic dye Reactive Brilliant Red K-2BP, *J. Hazard. Mater.* 164 (2009) 1098–1104.