



## Barium borosilicate glass as a matrix for the uptake of dyes

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### ABSTRACT

Barium borosilicate (BBS) and sodium borosilicate (SBS) glass samples, prepared by the conventional melt-quench method, were used for the uptake of Rhodamine 6G dye from aqueous solution. The experimental conditions were optimized to get maximum uptake and was found to be 0.4 mg of dye per gram of BBS glass sample. For the same network former to modifier ratio, barium borosilicate glasses are found to have improved extent of uptake for the dye molecules from aqueous solutions compared to sodium borosilicate glasses. Based on <sup>29</sup>Si MAS NMR studies on these glasses, it is inferred that significantly higher number of non-bridging oxygen atoms present in barium borosilicate glasses compared to sodium borosilicate glasses is responsible for its improved uptake of Rhodamine 6G dye. <sup>11</sup>B MAS NMR studies have confirmed the simultaneous existence of boron in BO<sub>3</sub> and BO<sub>4</sub> configurations in both barium borosilicate and sodium borosilicate glasses. The luminescence studies have established that the dye molecule is incorporated into the glass matrix through ion exchange mechanism by replacing the exchangeable ions like Na<sup>+</sup>/Ba<sup>2+</sup> attached with the non-bridging oxygen atoms present in the glass.

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### 1. Introduction

The industrial growth with changes in manufacturing processes has resulted in an increase in the volume and complexity of wastewater discharges to the environment [1]. Many traditional and novel treatment processes are being modified and developed to try to eliminate the release to surface waters of the diverse chemical substances found in wastewater discharges. The removal of coloured products from textile wastewaters has always been a worldwide problem for which various technologies have been used [2]. Different methods like adsorption, precipitation oxidation and reductions have been used for decolourizing the effluents. Ion exchange is a very versatile and effective tool for the treatment of aqueous hazardous wastes [3,4]. Unlike many other separation processes such as evaporation and reverse osmosis that remove the water from the polluting species, ion exchange usually removes the pollutants from the water. Since the pollutant is often present in low concentration, ion exchange is often more efficient for the treatment as compared to other processes.

Borosilicate glasses are technologically important due to their high mechanical strength and chemical durability and are widely

used in various applications. In nuclear industry it is mainly used as matrix for immobilizing the radioactive ions present in the waste generated from the nuclear reactors [5–8]. The structural elucidation of these glasses has been carried out using magic angle spinning nuclear magnetic resonance (MAS NMR), Raman and IR spectroscopy [9,10]. These studies show the existence of structural units like trigonally coordinated boron (BO<sub>3</sub>), tetrahedrally coordinated boron (BO<sub>4</sub>), silicon structural units having different number of bridging oxygen atoms (*Q<sup>n</sup>* denotes Si with *n* number of bridging oxygen atoms). Addition of network modifiers (alkali/alkaline earth metal oxides) to borosilicate glasses results in the conversion of BO<sub>3</sub> to BO<sub>4</sub> structural units. The (BO<sub>4</sub>)<sup>-</sup> and (SiO<sub>4</sub>)<sup>-</sup> structural units are charge neutralized by Na<sup>+</sup> ion, which can be replaced by other ions. In all the earlier studies using borosilicate glasses by different researchers [11,12], the metal ions were incorporated during the synthesis stage. However, in our earlier attempt, we have made use of barium borosilicate glass as ion exchanger at room temperature and studied its ion exchange property and separation efficiency with respect to uranyl ion [13,14]. Based on these studies, it was seen that barium borosilicate glass behaves like a good ion exchanger at room temperature. Therefore, it was proposed to study the uptake of some cationic dyes using this glass. There are earlier reports of dye being sorbed on to glass plate and glass fibres [15,16]. However, in the present work, we have taken base sodium borosilicate (SBS) glass without and with barium oxide as modifier (BBS) and carried out the uptake of Rhodamine 6G from aqueous

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solution at room temperature. In addition to studying the effect of various experimental factors on the uptake, the effect of composition of glass on the sorption characteristics has been studied and the difference in behaviour has been understood using structural characterization.

## 2. Experimental

### 2.1. Reagents

- (i)  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  of reagent grade
- (ii) Rhodamine 6G stock solutions: a stock solution was prepared by dissolving 0.1 g of dye in double distilled water and made up to 100 mL. From this stock solution, various concentrations of the dye solution were prepared using doubly distilled water.

### 2.2. Instrumentation

The absorbance measurements were done with a UV–vis double beam spectrophotometer equipped with a 1 cm quartz cell. The pH measurements were carried out using an EIL 7030 pH meter equipped with a combination electrode.  $^{29}\text{Si}$  and  $^{11}\text{B}$  MAS NMR patterns of these glasses were recorded using a NMR machine having a magnetic field of 7.04 T. Powdered samples were packed inside zirconia rotors and subjected to a spinning speed of 5 kHz. The luminescence studies were carried out using a fluorimeter having 150 W Xe lamp excitation source. Electron Probe Micro Analyzer was used for assessing chemical homogeneity of the glass samples. An acceleration voltage of 20 kV and 4–100 nA stabilized beam current was used for secondary and back scattered electron (BSE) imaging (with atomic number ( $Z$ ) contrast) and X-ray analysis respectively.

### 2.3. Procedure

#### 2.3.1. Synthesis and characterization of glass samples

Required amounts of analytical grade  $\text{NaNO}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$  were taken so as to get a glass with a composition  $(\text{SiO}_2)_{0.39}(\text{B}_2\text{O}_3)_{0.25}(\text{Na}_2\text{O})_{0.12}(\text{BaO})_{0.24}$ . The precursors were initially mixed together in siliminite crucibles, ground well and heated gradually to 1000 °C in an ordinary resistance furnace with air atmosphere and soaked for 4 h. The borosilicate melts were subsequently quenched on air cooled, cleaned stainless steel plates. The glass powders obtained are sieved using ASTM sieves of specific mesh size. The glass samples were characterized by NMR, luminescence and electron imaging techniques.

#### 2.3.2. Sorption studies

The uptake of Rhodamine 6G by glass powder was studied using a batch mode process at room temperature of 26 °C. 10 ml of aqueous dye solution of known concentration at a particular pH was equilibrated with a weighed amount of glass sample for different periods of time. The concentration of dye left behind in solution after equilibration was determined by measuring the absorbance at 547 nm.

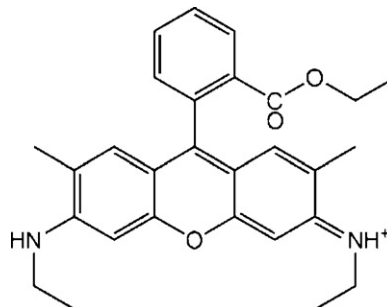
#### 2.3.3. Desorption studies

Several samples of the dye-loaded glass were prepared by taking a known amount of glass and fixed concentration of the dye solution. After equilibration, the glass was separated from the dye solution by centrifugation and then washed gently with water to remove any unabsorbed dye. Then these samples were equilibrated with 50 ml of distilled water, adjusted to different pH values. The desorbed dye solution was estimated as before.

**Table 1**

Molar composition of various components of the two glass samples.

	Mol %			
	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{BaO}$
SBS	53.53	30.30	16.17	–
BBS	47.34	26.80	14.30	11.56



**Fig. 1.** Structure of Rhodamine 6G.

## 3. Results and discussion

The structural formulae of barium borosilicate (BBS) and sodium borosilicate (SBS) glasses are  $[(\text{Na}_2\text{O})_{0.143}(\text{B}_2\text{O}_3)_{0.268}(\text{SiO}_2)_{0.473}(\text{BaO})_{0.116}]$  and  $[(\text{Na}_2\text{O})_{0.162}(\text{B}_2\text{O}_3)_{0.303}(\text{SiO}_2)_{0.535}]$ , respectively. The molar composition of the BBS and SBS are given in Table 1. The structure of Rhodamine 6G is shown in Fig. 1.

### 3.1. Synthesis and characterization of the glass samples

The glass samples were prepared by standardized procedures and hence it was expected that the surface area variation will be minimum. In the present studies, the powders were labelled as –70 + 80 ASTM. This indicated that the powders were sieved through sieves of different mesh sizes. In the present case, the glass powders passed through sieve of size 70 but were retained with sieve of size 80. From ASTM specifications, it is known that sieve 70 indicates particle size of 212  $\mu\text{m}$  whereas sieve 80 indicates particles of size of 180  $\mu\text{m}$ . Thus it was concluded that the particle size of the powders used in the present study was in the range of 180–212  $\mu\text{m}$ . The surface area measurement of these powders by BET method did not give correct and reproducible values. This could be due to the inhomogeneous adsorption of nitrogen over the glass surface and this is a common problem encountered with glass samples. Hence a simple alternative procedure was adopted for the calculation of surface area of the particles based on the assuming that all glass powders are spherical in size. The average particle size is calculated and it showed that the powders used in the present study have an average diameter of 196  $\mu\text{m}$  and hence the average radius is 98  $\mu\text{m}$ . The surface area was calculated using the equation given below wherein the  $r$  is the average diameter of the particles (98  $\mu\text{m}$ ) and  $\rho$  is the density of glass calculated using Archimedes principle and was found to be 3 g/cc.

$$\text{surface area (SA)} = \frac{4\pi r^2}{((4/3)\pi r^3 \rho)}$$

The surface area of the glass powders used in the present study was calculated to be 102  $\text{cm}^2/\text{g}$ . Moreover, in the present study, the glass powders used were all sieved using the same mesh size and further the surface area was not one of the varying parameters which was studied to get maximum uptake of dye.

The optical and back scattered electron images of the glass are given in Fig. 2. Both the images show that the base glass is

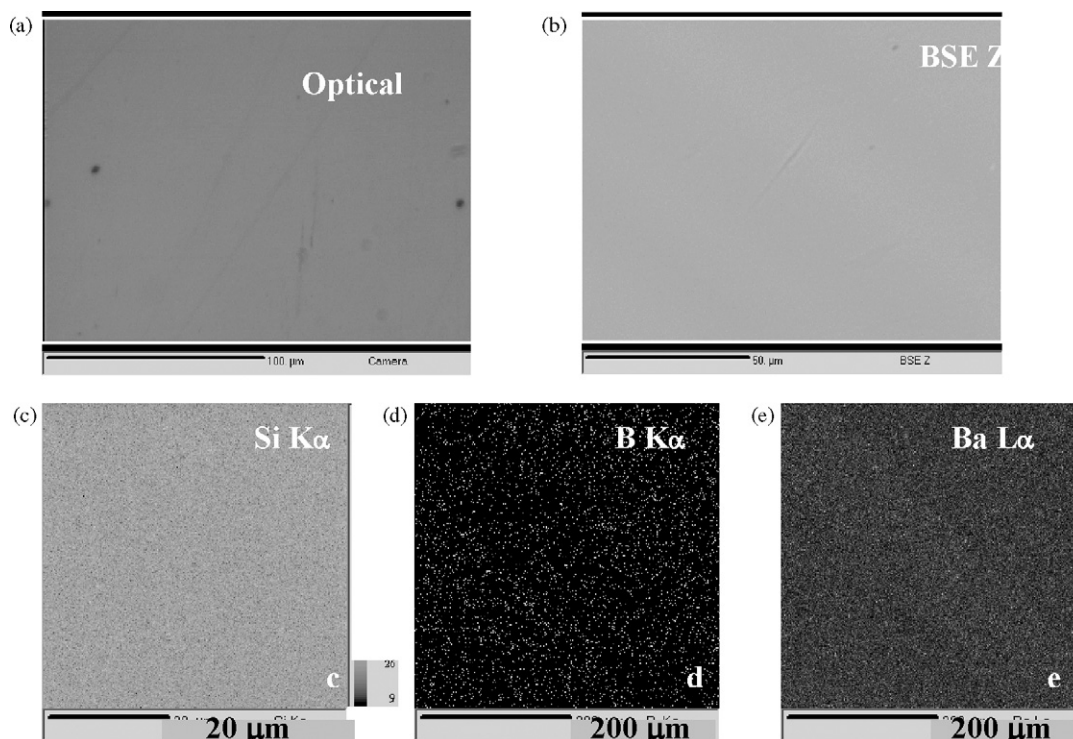


Fig. 2. (a) Optical, (b) BSE, (c) Si K $\alpha$  X-ray, (d) B K $\alpha$  X-ray and (e) Ba L $\alpha$  X-ray.

homogeneous in composition. The Si K $\alpha$ , B K $\alpha$  and Ba K $\alpha$  X-ray images (Fig. 2c–e) also clearly show that these elements are homogeneously distributed in the glass. The further characterization of glass samples was not within the scope of the present work.

### 3.2. Sorption studies

Various factors were studied to optimize the experimental conditions to get maximum uptake of Rhodamine 6G by the glass samples. The variation in experimental factors like contact time, pH, amount of glass were all studied using 1 mM dye solution.

#### 3.2.1. Effect of contact time

The effect of contact time on the uptake of dye is shown in Fig. 3. It is seen that within a period of 12 h, the uptake increases rapidly

and then almost reached the saturation. Further, it was observed that between 12 and 24 h of equilibration, the amount taken up is not much significantly different and therefore, optimum of 12 h is taken for all further experiments.

#### 3.2.2. Effect of pH of external solution

Since the dye is cationic in nature, it was expected that the pH of the external solution would have an effect on the uptake. The variation in the uptake with pH is shown in Fig. 4. It is seen that the amount of dye taken up by the glass increased with increase in pH to about a value of 6. Beyond pH 6, the increase in pH resulted in the decrease in the uptake. This could be due to the fact that at both the lower and higher pH the amount of dye available for the uptake study is reduced and also due to the presence of competing cations at higher concentration level. At lower pH, excess H<sup>+</sup> ions present

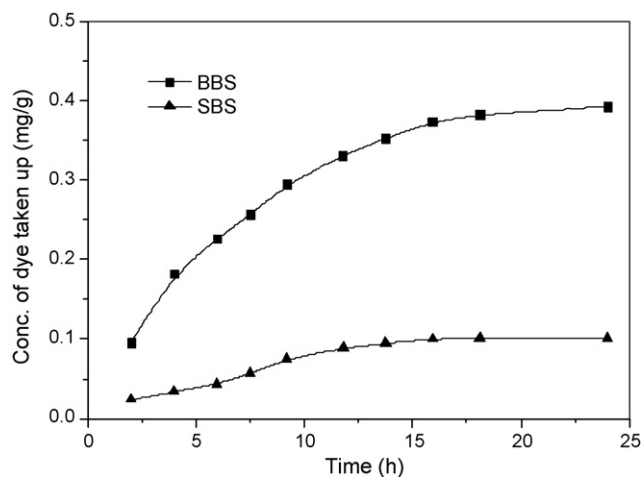


Fig. 3. Effect of contact time on the uptake of dye using 1 mM dye solution, 0.1 g of glass at room temperature of 26 °C at pH of 6.

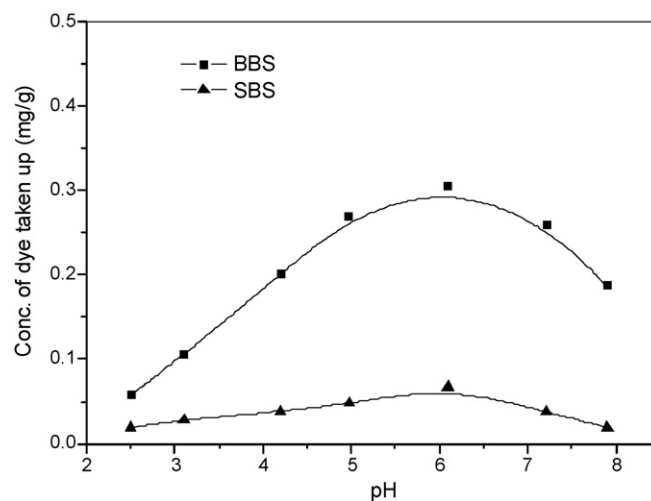


Fig. 4. Effect of pH on the uptake of dye using 1 mM dye solution, 0.1 g of glass at room temperature of 26 °C for a period of 12 h.

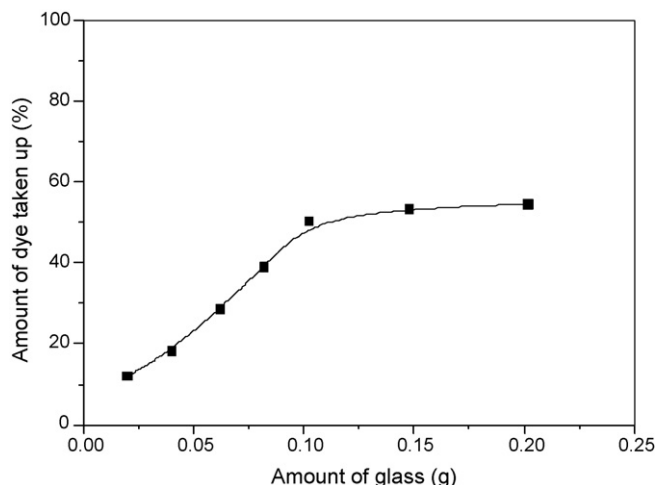


Fig. 5. Effect of amount of adsorbent on the uptake of dye using 1 mM dye solution at room temperature of 26 °C for a period of 12 h at pH of 6.

will compete with the dye cation for the adsorption sites. Moreover at lower pH, the amount of dye available is also lowered because of its chemical degradation to a lactone structure [17], which presents an unfavourable condition for the uptake. As the pH of the system increases, the concentration of the competing  $H^+$  ions decreases resulting in an increase in the uptake of the dye with increasing pH as the negatively charged sites are less protonated and available for the adsorption of dye cation, due to electrostatic attraction. This increase occurs till a pH value of 6 beyond, which a decrease in the amount taken up is observed. At a higher pH (>6), the dye exists as its neutral or anionic form and this cannot be taken up by the barium borosilicate glass, which behaves like a cation exchanger. Also at higher pH, there is excess of  $Na^+$  ions, which will compete with the uptake of the dye. Hence the pH was maintained at 6 for all further studies.

### 3.2.3. Effect of amount adsorbent dosage

The effect of amount of adsorbent on the uptake was studied by varying the amount of BBS glass in the range of 0.02–0.2 g. The results are shown in Fig. 5. From the figure, it is seen that there is a rapid increase in the amount taken up with an increase in the amount of adsorbent. This is expected because with the increase in the adsorbent amount, the ratio of the number of the adsorbent particles to dye cations increases. These results in more ions attached to the adsorbent surfaces. From the figure, it is seen that 0.1 g of glass was sufficient to bring about maximum uptake.

### 3.2.4. Effect of initial dye concentration

The effect of initial dye concentration was studied at pH 6 using 0.1 g of BBS for a period of 12 h equilibration. The results are shown in Fig. 6. It was observed that the amount taken up keeps increasing till a particular value and then the values reach saturation.

## 3.3. Structural elucidation

These were carried out to understand how the glass samples behave as ion exchangers and also the nature of interaction of the Rhodamine 6G with the glass structure.

### 3.3.1. Effect of nature of glass

From the variation studies of both pH and contact time shown in Figs. 2 and 3, it is seen that the two glasses BBS and SBS have different uptake capacities. It is observed that the exchange capacity of BBS is higher than that of SBS under all experimental conditions. To understand the differences in the ion exchange behaviour, the

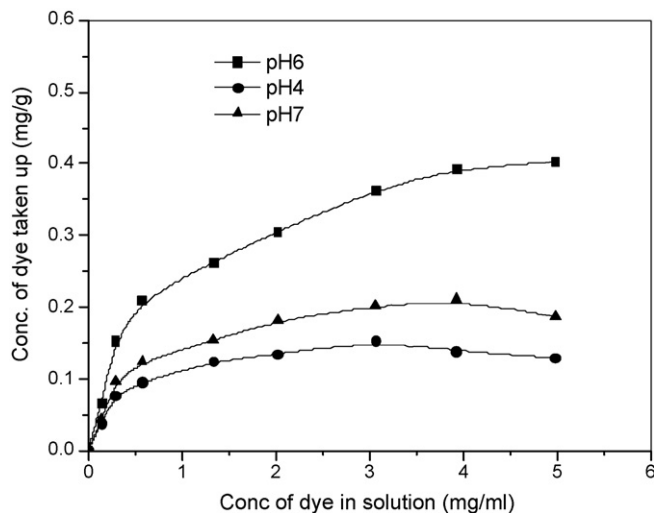


Fig. 6. Effect of initial dye concentration on the uptake under three different pH conditions using 0.1 g of BBS glass at room temperature of 26 °C for a period of 12 h.

structural aspects of both the glasses were considered. Rhodamine 6G is a cationic dye and the exchange by the glasses proceeds via cation exchange phenomena between the ions in the glass and the dye in solution. Hence the increased uptake by BBS implied that there are more numbers of exchangeable ions in BBS as compared to SBS. It is well known that the addition of network modifiers to a silicon network results in the conversion of  $Si-O-Si$  to  $Si-O^-Na^+$  or  $Si-O-H$  linkages thereby increasing the concentration of non-bridging oxygen atoms in the glass. To understand these differences, NMR studies of the two glasses were carried out and the results are shown in Fig. 7. From  $^{29}Si$  NMR, it is seen that pure silica contains silicon with bridging oxygen atoms represented  $Q^4$  structural units. On addition of alkali and alkaline earth metal oxides the  $Si-O-Si$  linkages breaks resulting in the formation of non-bridging oxygen atoms attached to silicon. Depending on the number of bridging oxygen atoms attached to silicon, each silicon unit can be represented as  $Q^2$ ,  $Q^3$ ,  $Q^4$ , etc. ( $Q^n$  represents number of bridging oxygen atoms). Most of the silicates contain  $Q^4$  structural units. All the patterns are characterized by broad asymmetric peak whose maxima systematically shifted towards more positive values with addition of BaO in the glass. The patterns were deconvoluted into individual components based on a Gaussian fit. For sodium borosilicate glass without any BaO,  $^{29}Si$  MAS NMR pattern could be deconvoluted into two peaks with chemical shift values around  $-99$  and  $-86$  ppm. Based on the previous  $^{29}Si$  MAS NMR studies on borosilicate glasses, the peak around  $-99$  ppm can be attributed to  $Q^3$  structural units and that around  $-86$  ppm can be attributed to  $Q^2$  structural units of silicon.  $^{29}Si$  MAS NMR studies have established that BaO addition is associated with a marginal increase in the concentration of  $Q^2$  structural units of silicon at the expense of  $Q^3$  structural units. The increase in chemical shift values of  $Q^3$  structural units has been attributed to the preferential interaction of higher field strength  $Ba^{2+}$  ions with the non-bridging oxygen atoms of the  $Q^3$  structural units. The possible reason for this could be the more covalent nature of  $Q^3$  structural units compared to  $Q^2$  structural units. The non-bridging oxygen atoms of the silicon network are charge neutralized by the presence of  $Na^+$  ions. It is these  $Na^+$  ions, which are exchanged with dye cations. Hence the presence of more non-bridging oxygen atoms results in increase in the ion exchange property.  $^{11}B$  MAS NMR patterns shown in Fig. 3 consist of sharp peak characteristic of  $BO_4$  structural units and broad peak corresponding to  $BO_3$  structural units. The sharp peak is superimposed over broad shoulders placed symmetrically on either sides of the sharp peak. The sharp peak is attributed to the tetrahedrally

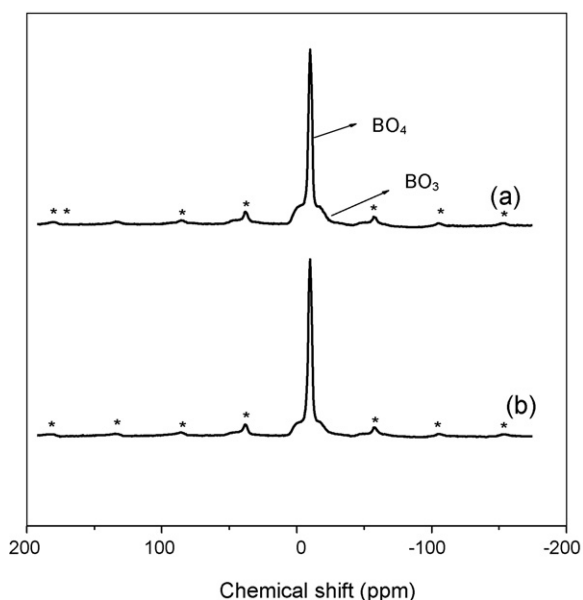
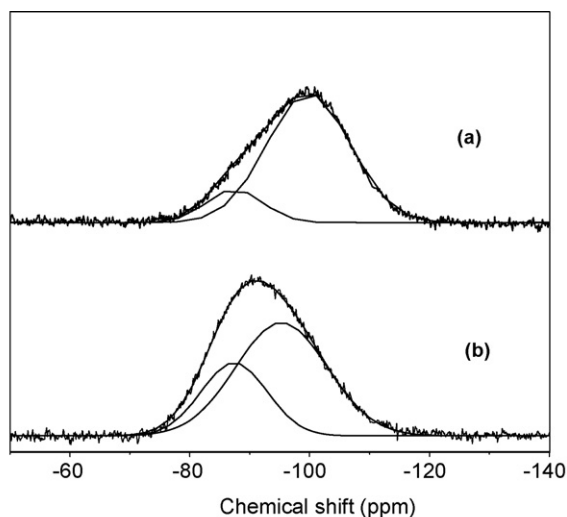


Fig. 7. MAS NMR spectra of (a) SBS and (b) BBS glass samples.

coordinated boron ( $\text{BO}_4$ ) structural units and broad peak to the trigonally coordinated boron ( $\text{BO}_3$ ) structural units. The line shape and peak position are identical for all the glass samples. As  $^{11}\text{B}$  is a quadrupolar nuclei ( $I = 3/2$ ), it will be having a negligible quadrupolar interaction when it occupies environment with cubic symmetry, i.e. tetrahedrally coordinated boron structural units ( $\text{BO}_4$ ). Unlike this boron in trigonal coordination ( $\text{BO}_3$  structural units) is significantly affected by the quadrupolar interaction thus resulting in the appearance of a broad peak. NMR patterns showed that relative concentration of  $\text{BO}_3$  and  $\text{BO}_4$  structural units are unaffected by  $\text{BaO}$  incorporation in the glass. From these results it can be confirmed that the  $\text{Ba}^{2+}$  ions have got no direct interaction with boron structural units in the glass. Boron in these glasses exists only as  $\text{BO}_4^-$  structural units whose charge is neutralized by the  $\text{Na}^+$  ions. The increase in the amount of exchangeable ion ( $\text{Na}^+$ ) results in the increased ion exchange capacity of BBS as compared to SBS.

### 3.3.2. Interaction of dye with the matrix

To confirm that the dye taken up is bound to the glass, luminescence study was carried out using the dye incorporated BBS. The results are shown in Fig. 8. It is seen that the dye in solution shows a maximum at 545 nm whereas on incorporation into the

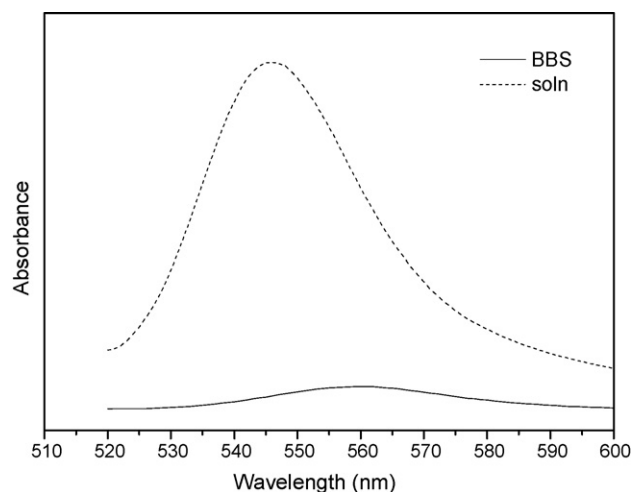


Fig. 8. Emission spectra of the dye in solution and loaded on BBS.

glass matrix the maxima is red shifted to 558 nm. The maxima at 545 nm is due to the  $n-\pi^*$  transitions. Due to exchange of the dye with the glass, there is an interaction between the cationic dye and the oxygen atoms present in the glass. This electrostatic interaction results in the decrease in the energy levels and hence the absorption maximum is shifted on exchange.

### 3.4. Desorption studies

The effect of pH on the trend of desorption studies is just opposite to that of adsorption process. It is seen that the percent desorption increased from 62.6 to 80.7 with decrease in pH from 8.5 to 2. The reversal in the trend of desorption as compared to that of adsorption indicated that the uptake of the Rhodamine 6G dye is mainly due to ion exchange.

### 3.5. Data analysis

#### 3.5.1. Equilibrium modelling

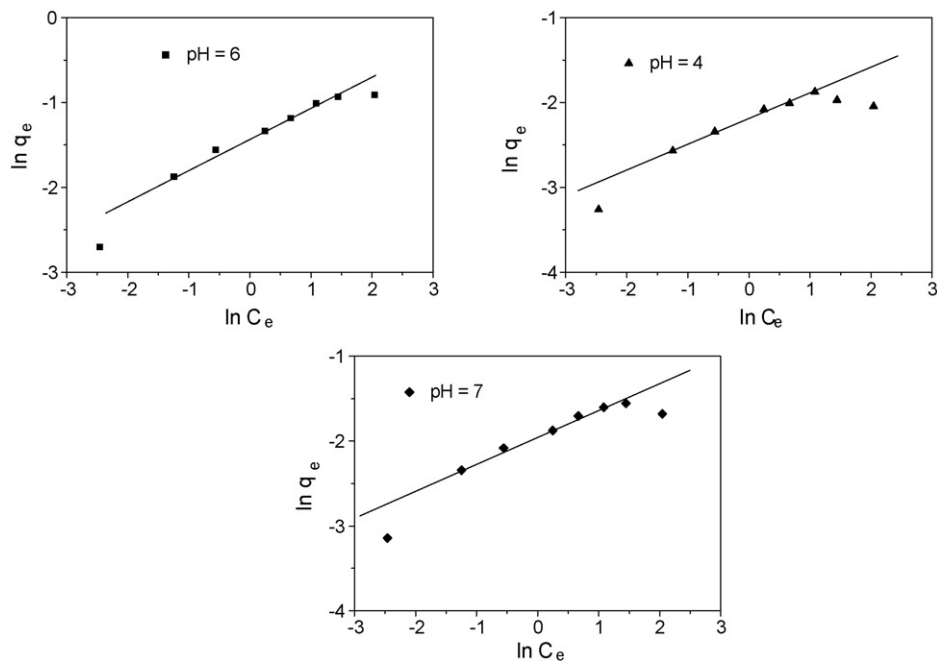
The main scope of the present study is to apply the glasses as room temperature ion exchangers. Therefore the results obtained for maximum uptake of the dye at optimized experimental conditions of pH, amount of glass, etc. at room temperature were fitted to the Langmuir and Freundlich adsorption models. For this, the amount of dye taken up by the glass is calculated by the simple concentration difference method. The batch mode experiments are carried out with  $W$  g of glass and  $V$  ml of the dye solution. If the initial and final concentrations of dye are  $C_0$  and  $C_t$  (mg/ml), the dye uptake  $q$  (mg/g) is calculated from the mass balance using Eq. (1) given below.

$$q = \frac{(C_0 - C_t) * V}{W * 1000} \quad (1)$$

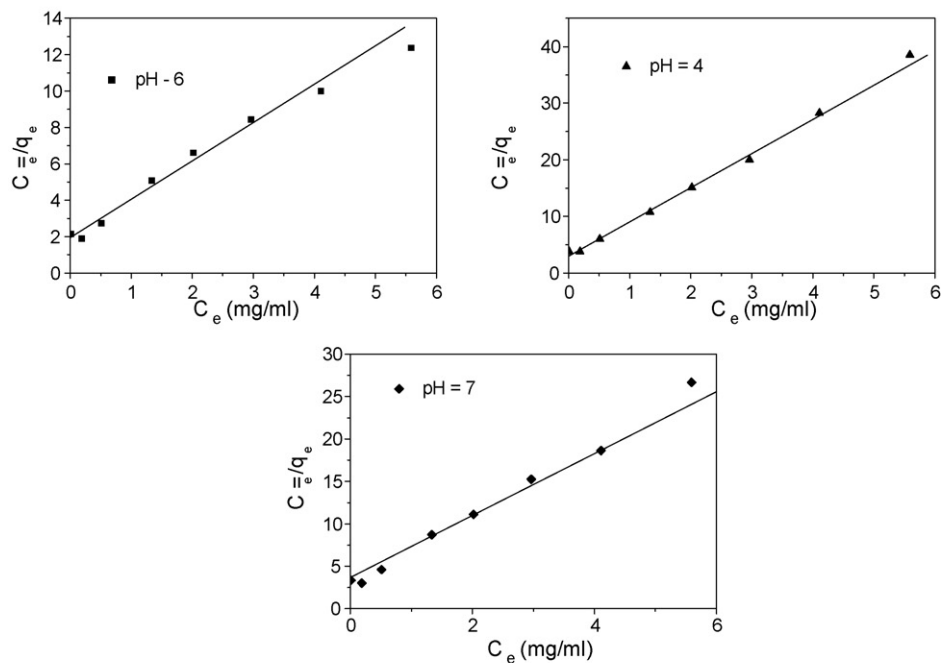
The linearised form of Freundlich equation is given in (2), where,  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration (mg/ml).  $K_f$  and  $n$  are constants indicative of adsorption capacity and adsorption intensity, respectively.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

The Langmuir equation assumes that: (i) the solid surface presents a finite number of identical sites which are energetically uniform; (ii) there are no interactions between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption and (iii) a monolayer is formed when the solid surface reaches saturation. The linear form of Langmuir equation is given in Eq. (3),



(a) Freundlich plots at different pH values



(b) Langmuir plots at different pH values

**Fig. 9.** Langmuir and Freundlich plots for adsorption (values of  $C_e$  is in mg/ml and that of  $q_e$  in mg/g).

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration (mg/ml),  $b$  is a constant related to the energy and  $Q^0$  is the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g).  $Q^0$  represents a practical limiting adsorption capacity when the surface is fully covered with dye cations. By plotting  $(C_e/q_e)$  versus  $C_e$ ,  $Q^0$  and  $b$  can be determined if a straight line is obtained.

$$\frac{C_e}{q_e} = \frac{1}{Q^0 * b} + \frac{C_e}{Q^0} \quad (3)$$

The results of the equilibrium modelling for the present study is given in Fig. 9. Values of  $Q^0$  and  $b$  were calculated from the slope and intercept of the linear plots and are presented in Table 2. The values obtained from this analysis showed that the adsorption of dye followed both Langmuir and Freundlich type of isotherms. The applicability of the Langmuir isotherm suggests the monolayer coverage of the dye on the glass surface. If the value of Freundlich constant  $n$  lies in between 1 and 10, it indicates a favourable adsorption [18] and in the present study it is seen that the adsorption is favoured as shown by the values of  $n$ . However, the low values of  $K_f$

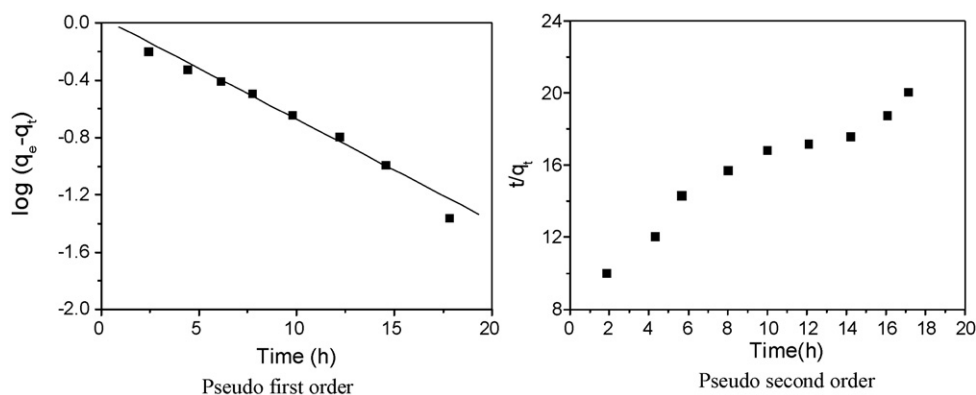


Fig. 10. Reaction kinetic models for uptake of Rhodamine 6G using 0.1 g of BBS at pH of 6.

Table 2

Values from Langmuir and Freundlich Isotherms at different pH using 0.1 g of BBS glass for a equilibration time of 12 h.

pH	Langmuir constants		Freundlich constants	
	$Q^0$ (mg/g)	$b$ (ml/mg)	$K_f$	$n$
4	0.165	2.04	0.11	3.3
6	0.498	1.15	0.238	3.15
7	0.274	0.99	0.141	3.12

indicate the slow kinetics of the sorption by the glass samples. It is seen that the values are dependent of the pH of the external solution indicating that the uptake follows an ion exchange mechanism.

### 3.5.2. Reaction-based models

The pseudo-first-order model proposed by Lagergren and pseudo-second-order model proposed by Ho and Mackay, were employed to explain the solid/liquid adsorption. It was Lagergren who first presented the first-order rate equation for the adsorption [19] and thereafter it has been extensively used for the adsorption of an adsorbate from an aqueous solution. In order to distinguish the kinetics equation based on the adsorption capacity of solid from the concentration of solution, Lagergren's first-order rate equation has been called pseudo-first-order since 1998 [20]. A second-order kinetic expression for the adsorption was reported by Ho. In order to distinguish the kinetic equation based on the adsorption capacity of solid from the one that is based on the concentration of solution, Ho's second-order rate expression has been called pseudo-second-order [21].

(i) Pseudo-first-order kinetic model is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{(k_{ad} * t)}{2.303}$$

where  $q_e$  and  $q_t$  are the amount of Rhodamine 6G on the surface of the sorbent beads (mmol/g) at equilibrium and at time  $t$  respectively and  $k_{ad}$  is the equilibrium rate constant of pseudo-first-order sorption ( $\text{h}^{-1}$ ). The slope of the straight line plot of  $\log(q_e - q_t)$  against  $t$  will give the values of the rate constants ( $k_{ad}$ ).

Pseudo-second-order model is expressed linearly by the following equation,

$$\frac{t}{q_t} = \frac{1}{K_{2ads}q_e^2} + \frac{t}{q_e}$$

where  $q_t$  is the amount of Rhodamine 6G on the surface of the bead (mmol/g) at any time  $t$ ,  $K_{2ads}$  is the pseudo-second-order

rate constant ( $\text{g}/\text{mmol h}$ ) and  $q_e$  is the amount of Rhodamine 6G sorbed at equilibrium (mmol/g) and the initial sorption rate. The data obtained is fitted in a plot  $t/q_t$  against  $t$  which should be a straight line and the values of  $q_e$  and  $K_{2ads}$  can be calculated from the slope and intercept respectively.

Fig. 10 shows the results of the data analysis using the two kinetics models for the uptake of Rhodamine 6G using BBS glass at optimized experimental conditions. It is seen that the uptake of Rhodamine 6G follows the pseudo-first-order kinetics as compared to the pseudo-second-order. The value of  $q_e$  obtained is 0.91 mmol/g and the rate constant is calculated as  $0.163 \text{ h}^{-1}$ . The value of  $q_e$  gives the maximum amount of the dye that can be taken up and the calculated value is in correlation with the maximum amount obtained experimentally and also from the data treatment using Langmuir equation.

## 4. Conclusion

The present study shows that the barium borosilicate glass is an effective adsorbent for the removal of Rhodamine 6G from aqueous solution. The present study shows that though the sorption capacity of glass is low, it appears as an attractive and cheap adsorbent. The possibility of using glasses as adsorbents makes the process attractive as the waste generated from used glass can also have a potential use. However, the main aim of the present work was to demonstrate the adsorption capability of the glass samples and to carry out structural elucidation to understand the sorption behaviour of glass. Adsorption of the dye molecule follows both Langmuir and Freundlich isotherms. The reversal in the trend of desorption as compared to that of adsorption indicated that the uptake of the Rhodamine 6G dye follows an ion exchange mechanism. Desorption studies do indicate the potential reusability of the glass powders. Exchangeable ions like  $\text{Na}^+/\text{Ba}^{2+}$  ions attached with the non-bridging oxygen atoms present in the glass are replaced by the dye molecule during the ion exchange process. The reaction rate constant is  $0.163 \text{ h}^{-1}$  and the maximum amount of dye taken up is about 0.9 mmol/g as obtained from the results of both equilibrium modelling and reaction based models. Based on the  $^{29}\text{Si}$  MAS NMR studies, it is concluded that increase in number of non-bridging oxygen atoms present in barium borosilicate glass compared to sodium borosilicate glass is responsible for its improved dye uptake characteristics. Boron in these glasses exist in both  $\text{BO}_3$  and  $\text{BO}_4$  structural units as revealed by the  $^{11}\text{B}$  MAS NMR studies. The main aspect of this work was to demonstrate that glass powders do possess ion exchange capacity for organic dyes and correlate it to the structural aspects. Desorption studies were carried out to explore the possibility of reuse of the glass as adsorbents. This work will

have more potential applications when used in a column. These initial studies in batch mode show the possible application of glasses as simple adsorbents. In order to make it feasible for actual applications, further studies need to be carried out.

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