Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.2179

40 (2012) 15–23
February

Preparation and characterization of imino diacetic acid functionalized alginate beads for removal of contaminants from waste water: I. methylene blue cationic dye model

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Received 29 July 2010; Accepted 22 December 2011

ABSTRACT

This study deals with the development of a clean and safe process for water pollution remediation. We studied the potential use of Imino Diacetic Acid (IDA) activated calcium alginate beads for removal of cationic dyes from colored effluents in dynamic batch mode. Methylene blue (MB) has been chosen as a dye model for the study. The parameters that affect the beads surface modification process such as ρ-benzoquinone (PBQ) and IDA concentration, reaction time, pH, temperature and finally cross linking time in calcium chloride solution were studied. Maximum percents of dye removal are about 65% and 90% were achieved at initial MB concentration of 50 mg l^{-1} after 60 min of adsorption at temperature (22 ± 1°C) for calcium alginate and IDA activated calcium alginate beads respectively. Surface modification reduces the competitive action of calcium ions especially at high bead's crosslinking degree. Removal percentage was doubled using modified alginate beads cross linked for 120 min at 2% $CaCl_2$. In conclusion, the modified alginate beads show higher affinity towards MB adsorption where removed 80% of the dye content after only 10 min compared with 48% for the unmodified beads. Regeneration of the beads was also tested and fast process was observed which provide us with possibility of reuse.

Keywords: Dye removal; Alginate beads; Adsorption; Methylene blue; Surface modification; Hydrogel

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1. Introduction

Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. There are more than 100,000 kinds of commercially available dyes with over 7×10^5 tonnes of dyes produced annually [1]. It is estimated that 2% of dyes produced annually are discharged in effluent from manufacturing operations, while 10% is discharged from textile and associated industries [2]. Adsorption process/technique is widely used in the removal of contaminants from wastewaters. Liquid–solid adsorption operations are concerned with the ability of certain solids to preferentially concentrate specific substances from solution onto their surfaces [3]. Alginate is one of the most extensively investigated biopolymers for removal of pollutants from aqueous solution as it is inexpensive, non-toxic and efficient. It is a natural polysaccharide extracted from brown seaweeds. This linear polymer is composed of b-D-mannuronate (M) and a-L-guluronate (G) units linked by b-1,4 and a-1,4 glycosidic bonds. M and G units are organized in MM, GG and MG blocks, the proportion of these blocks varying with the source of the polymer. Alginate beads are a common and well-known support material in bioscience application for immobilization of enzymes [4] and living cells [5]. In the environmental field, alginate beads have been used for the removal of some heavy metal ions.

Indeed carboxylate functions of this polysaccharide are negatively charged in neutral and alkaline media and hence have greater affinity to cations. For example, Pandey and Pandey [6] have used calcium alginate beads with and without humic acid for the removal of various metals; Jang and Nguyen [7] used Na-alginate to recover copper; by a treatment of Caalginate gel beads with Fe(III), Min and Hering [8] removed arsenic, chromium and selenium from wastewater. Besides, various alginate gel-based adsorbents were investigated by Hyun Gyu Park [9] for the removal of Pb(II): alginate beads and alginate gel-coated adsorbent prepared by forming a thin alginate film on an inert matrix (paper or cotton). Alginic acid has also been shown to be effective at removing many cationic metals from solutions including Pb(II), Cu(II), Cd(II), Zn(II), Co(II) [7,10,11]. The use of alginate beads for removal of organic pollutants has been also reported: Aravindhan and Fathima [12] have studied the removal of dyes from commercial tannery effluents by calcium alginate beads; Nasr and El-Ola [13] have compared the adsorption behavior of activated carbon (AC) fiber and modified alginate toward basic dyes. Recently, Vincent Rocher et al. [14] present the preparation of alginate beads containing commercially available AC and magnetic iron oxide nanoparticles. These beads were carefully characterized and their adsorption capacity toward basic dyes, positively charged MB and negatively charged methyl orange (MO), was compared with that of non-encapsulated AC.

In this work, we present a chemical route for the preparation of IDA activated alginate beads containing grafted carboxylic groups on its surface. These beads were carefully characterized and the impact of different factors controlling the surface modification process such as PBQ and IDA concentration, reaction time, pH, temperature and finally cross linking time in calcium chloride solution were studied. Their adsorption capacity for the removal of MB was compared with that of non-modified alginate beads.

2. Materials and methods

2.1. Materials

Cationic MB dye, C16H18N3SCl.3H2O, supplied from (NICE CHEMICALS Pvt. Ltd., COCHIN). The stock dye solution was prepared by dissolving 50 mg of MB in 1000 ml distilled water to obtain 50 mg l^{-1} initial dye concentrations. Sodium alginate (NaALG) with a medium viscosity was supplied from Sigma-Aldrich Company. Calcium chloride ($CaCl_2$) was supplied from Riedel-de Hean Company.

2.2. Methods

2.2.1. Beads preparation

Two percentage of sodium alginate solution was prepared by dissolving 2 gm of sodium alginate in 100 ml of hot distilled water with stirring until the solution become homogenous. For preparation of beads, 20 ml of 2% sodium alginate solution taken by 25 ml injection syringe and was added drop-by-drop into 2% calcium chloride solution at room temperature with genteel stirring. The formed beads were left to harden for 10 min. The beads were collected and then washed with distilled water several times to remove unbound calcium chloride from beads surface. The bead's diameter was experimentally estimated and found to be 3.5 mm.

To prepare the IDA activated beads, alginate beads prepared in the previous step were transfer to 100 ml beaker containing PBQ solution with definite concentration and pH. The beads left to react with PBQ for preselected time at designed temperature. After completion the reaction, PBQ activated beads were filtered and washed with distilled water to remove un-reacted PBQ. The PBQ activated alginate beads were transfer to 100 ml beaker containing IDA solution with definite concentration and pH. The PBQ activated beads left to react with IDA for preselected time at designed temperature. After completion the reaction, Alginate-IDA activated beads were filtered and washed with distilled water to remove un-reacted IDA.

2.2.2. Dye adsorption

Alginate beads (20 ml; 0.4 g dry weight) were mixed with 100 ml dye solution of 50 mg l^{-1} at room temperature. Adsorption experiments were conducted using a mechanical stirrer at 250 rpm. Sample of 0.5 ml was drawn at time intervals 5 min for 60 min and placed in test tubes adding to it 1.5 ml distilled water to be further analyzed by spectrophotometer.

The concentration of MB remaining in the supernatant after and before adsorption was determined with a 1.0 cm light path quartz cells using spectrophotometer at λ max of 665 nm. Prior to the measurement, a calibration curve was obtained by using the standard MB solution with known concentrations.

The %dye removal is calculated for each sample according to the following relation:

$$\%\ \text{dyes removal} = \left(1 - C/C_0\right) \times 100$$

where C_0 is the initial concentration of the dye. C is the concentration at time t.

To study the effect of a certain variable on the uptake of the dye, all the other variables are fixed throughout the experiments.

2.2.3. Dye desorption

Alginate beads with adsorbed MB were mixed with 100 ml NaCl solution dissolved at DW of variant concentration (1–3%) at room temperature. Desorption experiments were conducted using a mechanical stirrer at 250 rpm for 60 min. Sample of 0.5 ml was drawn at time intervals 5 min and placed in test tubes adding to it 1.5 ml distilled water to be further analyzed by spectrophotometer.

The concentration of MB released in the saline solution after desorption was determined as mentioned previously.

The MB regeneration percentage (%) was calculated for each sample according to the following relation:

$$\text{MB regeneration percentage}\,(\%) = \left(C_D/C_A\right) \times 100$$

where C_A is the amount of the adsorbed MB dye. C_D is the amount of the desorbed at time t.

To study the effect of a regeneration cycles on the MB desorption, all the variables are fixed throughout the repeated experiments.

2.2.4. Beads characterization

2.2.4.1. FT-IR spectroscopic analysis The structure of the alginate and alginate-PBQ-IDA modified beads were analyzed by FT-IR spectra. Samples were mixed with KBr to make pellets. FT-IR spectra in the transmittance mode were recorded using FT-IR spectrometer (Shimadzu FTIR- 8400 S, Japan), connected to a PC, and analysis the data by IR Solution software, Version 1.21.

2.2.4.2. Thermal gravimetric analysis The thermal degradation behaviors of the alginate and alginate-PBQ-IDA modified beads were studied using Thermo Gravimetric Analyzer (Shimadzu TGA – 50, Japan); instrument in the temperature range from 20°C to 600°C under nitrogen at a flow rate of 20 ml min^{-1} and at a heating rate of 10°C min^{-1}.

2.2.4.3. Morphological characterization (SEM) The surface morphology of alginate and alginate-PBQ-IDA modified beads were observed with the help of a scanning electron microscopy (Joel Jsm 6360LA, Japan) at an accelerated voltage of 20 kV. The fracture surfaces were vacuum coated with gold for SEM.

3. Results and discussion

3.1. Alginate beads activation with PBQ

Hydroxyl groups of alginate glucose ring backbone were activated through reaction with PBQ under studied reaction conditions. The impact of such activation step on the amount of introduced carboxylic groups through further reaction of PBQ activated alginate beads with IDA was followed by measuring changes in dye removal percentage compared with unmodified alginate beads. Factors such as PBQ concentration, reaction temperature, pH and time were investigated. The obtained results are discussed in the following.

Fig. 1 shows the effect of variation PBQ concentration on the percentage of MB removal. From the figure it is illustrated that all the PBQ activated beads have affinity for dye adsorption higher that the native beads. Indeed, variation of reacted PBQ concentration does not affect significantly the percentage of MB removal. Maximum removal percentage was found as 82% for PBQ activated alginate beads compared to 65% of native ones.

Variation of reaction temperature with PBQ from 20°C to 60°C has no significant effect on the capacity of PBQ activated alginate beads to adsorb MB dye. Still the facts that PBQ activated alginate beads under any reaction temperature have higher capability for MB dye removal. Removal capacity has been improved by about 25% referred to native alginate beads.

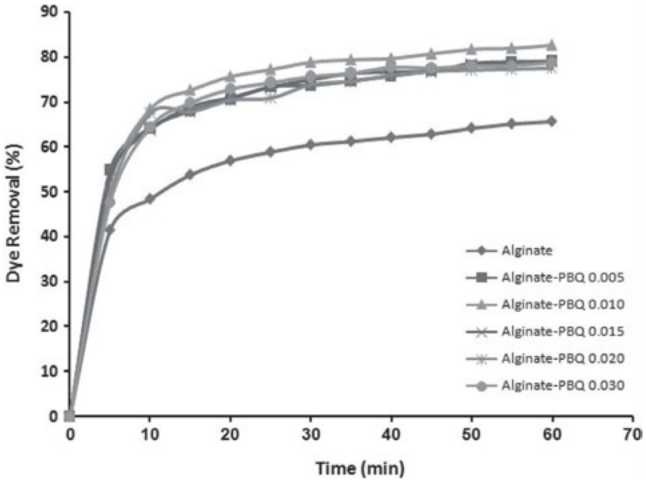


Fig. 1. Effect of PBQ concentration variation on dye removal (%) of alginate and modified alginate beads.

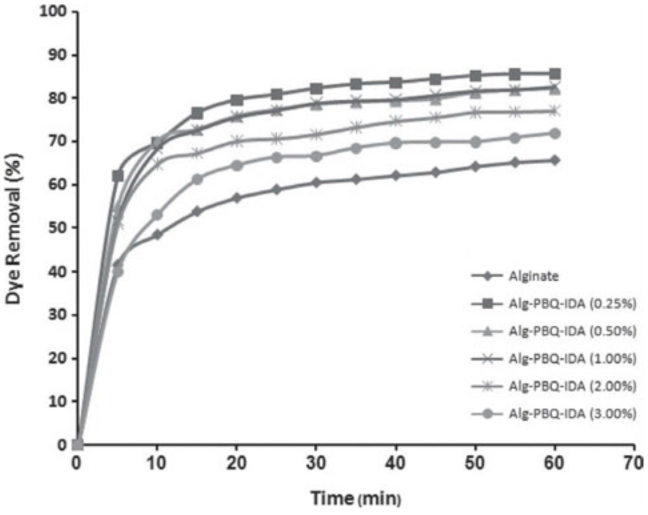


Fig. 2. Effect of IDA concentration variation on dye removal (%) of alginate and modified alginate beads.

The results obtained from investigation of the variation of reaction time with PBQ showed that 5 min are enough to have the maximum percentage of MB dye removal. Further prolongation of reaction time up to 60 min was found of neglect able effect.

From previous investigations by other groups it was found that the amount of attached PBQ to OH groups increased in alkaline reaction medium [15,16]. Accordingly, the effect of variation reaction medium pH from 4 to 12 was investigated. From the obtained results it was found that very slight changes could be observed upon variation of reaction medium pH. Again it is necessary to assure that all modified beads under any pH have higher affinity for MB adsorption.

From the previous obtained results of variation of reaction conditions with PBQ it is clear that the adsorption capacity for MB dye was improved under very mild conditions; very small PBQ concentration, room temperature, short reaction time and neutral pH which considered as an advantage. This behavior could be explained by occurrences of the reaction on the surface of the alginate beads.

3.2. *Carboxylation of PBQ activated alginate beads*

Now alginate beads with activated OH groups were prepared in the previous step and ready to react with IDA to functionalize its surface with carboxylic groups. Different parameters affecting the functionalization process are going to be studied in the following and its impact on the capacity of the alginate modified beads with carboxylic groups for adsorbing MB dye from solution will be monitored.

Variation of IDA concentration was found of pounced effect on the MB removal percentage (Fig. 2). Inspection of Fig. 2 reveled that all modified beads with IDA have higher affinity towards MB in respect to native alginate beads. In addition, it was found that the percentage of MB removal decreases with increase IDA concentration.

Alginate modified beads with minimum IDA concentration (0.25%) shows maximum MB dye removal; 87%, while with 3% IDA the removal percentage was found decreased to 70%. Native alginate beads show the minimum removal percentage; 65%.

Negative impact of elevation reaction temperature with IDA was observed in Fig. 3. From illustrated results it is obvious that conduction the reaction at minimum temperature, 20°C, shows maximum percentage of MB removal; 82%. Increase the reaction temperature up to 60°C, reduces the dye removal percentage to 70%.

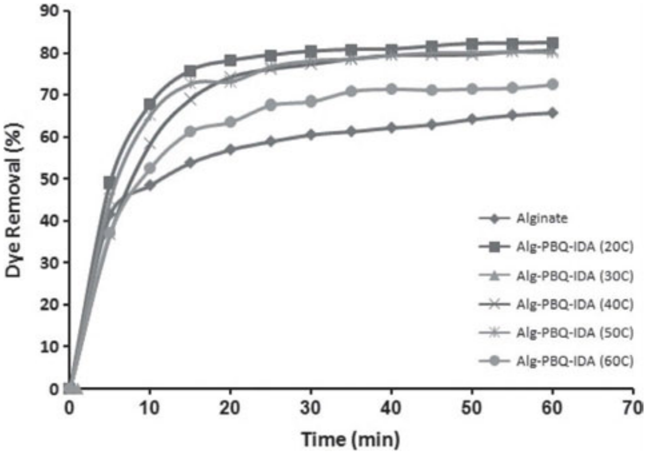


Fig. 3. Effect of variation reaction temperature with IDA on dye removal (%) of alginate and modified alginate beads.

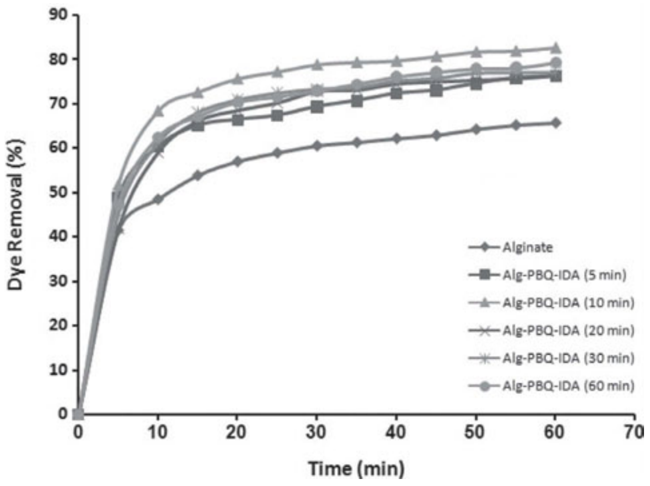


Fig. 4. Effect of variation reaction time with IDA on dye removal (%) of alginate and modified alginate beads.

Ten minutes of reaction with IDA was found as optimum reaction time where almost 82% of dye was removed after 30 min (Fig. 4). Increasing reaction time up to 60 min has no significant effect. The removal percentage is almost unaffected.

Preceding the reaction at pH range from 4 to 10 has no effect on variation the removal percentage; 78%, as seen in Fig. 5. The removal percentage increases to 87% with preceding the reaction at pH 12. It is worth to mention here that 80% of MB dye was removed after only 10 min.

3.3. Calcium ions competition effect

The negative charge carboxylate groups on alginate structure acting as active site for adsorbing MB through opposite charge attraction. In the same time the carboxylate groups incorporate in the ion cross linking gelation process to form the beads with calcium ions. Such competition behavior between calcium ions and MB molecules is clear with variation of cross linking time of the beads (Fig. 6). Increasing the cross linking time more than 10 min reduces significantly the dye removal percentage for native alginate beads. This effect was recognized much less with IDA activated beads. Such difference in respond to variation of cross linking time refereed to the dedication of introduced IDA carboxylic groups to the adsorption process of MB molecules in contrary to the native carboxylic groups of alginate. Another advantage of IDA carboxylic groups is its position on the surface of the beads which enables it from reaching easily the MB molecules in the bulk solution excluding the diffusion limiting step in the gel structure of the beads.

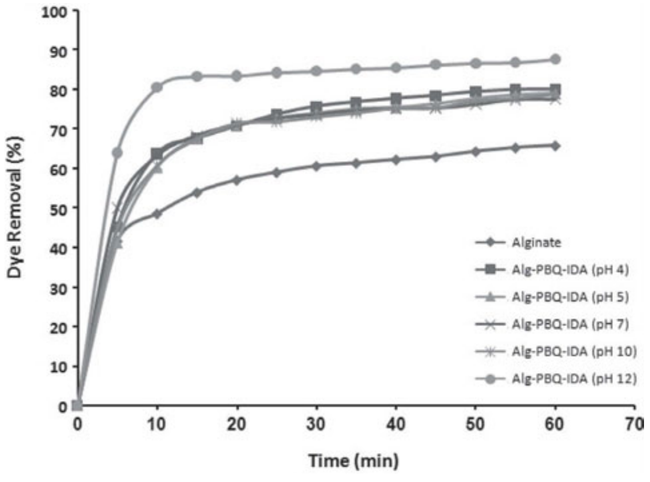


Fig. 5. Effect of variation reaction medium pH with IDA on dye removal (%) of alginate and modified alginate beads.

3.4. Desorption study

Desorption experiments were performed with the purpose of reusing the adsorbents and also to understand the mechanism of adsorption.

If the dye adsorbed onto the adsorbent can be desorbed by water, it can be concluded that the attachment of the dye onto the adsorbent is by weak bonds. If the strong acids, such as HCl can desorb the dye, it can be concluded that the attachment of the dye onto the adsorbent is by ion exchange or electrostatic attraction [17].

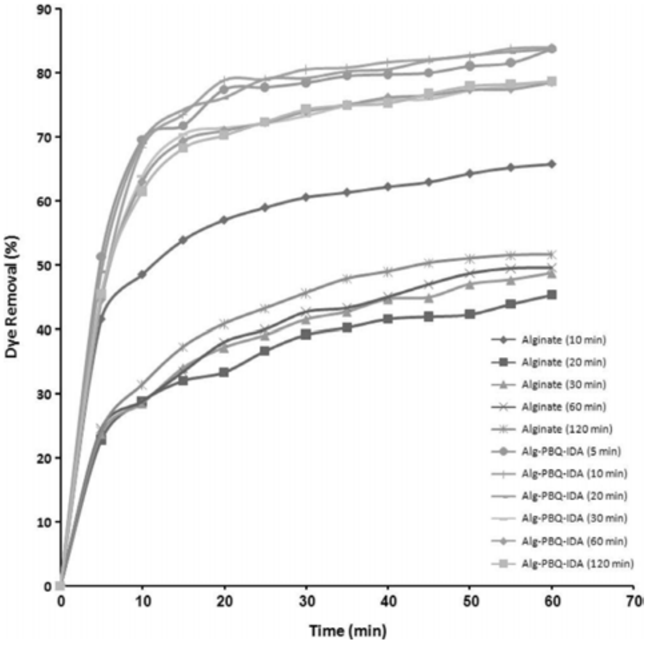


Fig. 6. Effect of variation crosslinking time with $CaCl_2$ on dye removal (%) of alginate and modified alginate beads.

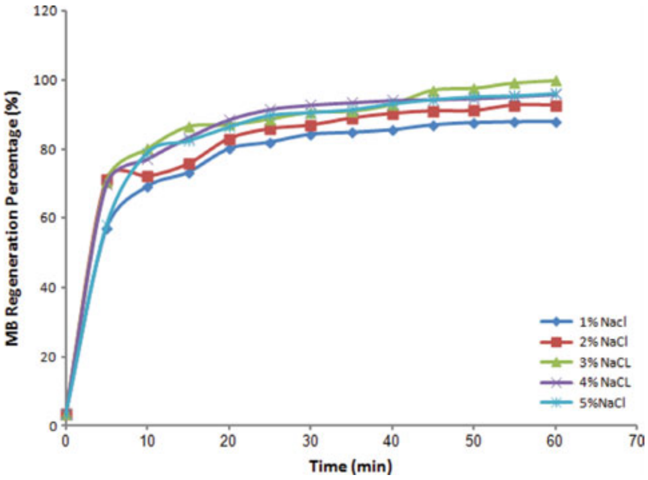


Fig. 7. Effect of NaCl concentration on MB regeneration percentage.

Desorption of MB using NaCl solution of different concentration was tried and the data are presented in Fig. 7. From the figure it is clear that very fast desorption of MB has been observed only within 5 min where 55–70% of adsorbed MB was detected in eluting solution. At equilibrium, the MB desorption percentage was ranged from 87% to 98% after 60 min. It is worthy to mention that water does not desorbe the adsorbed MB which means that the attachment of the dye onto the adsorbent is by ion exchange or electrostatic attraction [17].

The main goal of regeneration process is to reuse the adsorbent materials for many times as much as possible. Cycles of desorption have been tried under the same conditions using 1%, 2%, and 3% NaCl solution (Fig. 8). It is clear from the figure that gradual decreases of the MB desorption percentage has been observed using any NaCl concentration. The regeneration percentage tends to leveling off using lower concentrations of NaCl. It was observed that beads lost their mechanical properties along with cycles of regeneration. This effect was more clearly using higher NaCl concentration; 3%, where beads disintegrated after the third cycles. Less effect was noticed with lower NaCl concentrations, 1–2%, where the beads' mechanical properties last for higher number of reuse cycles.

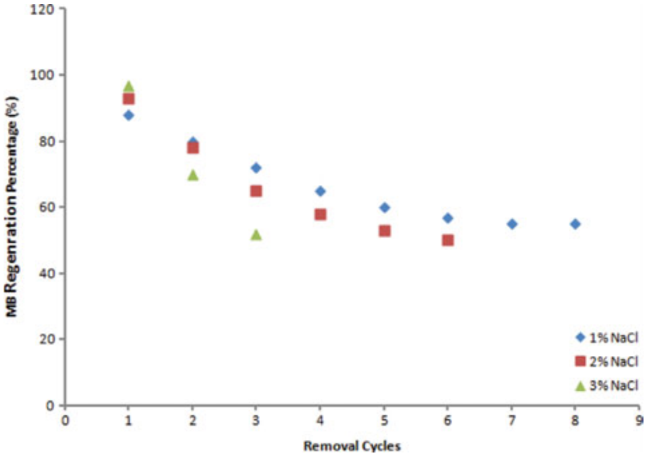


Fig. 8. Effect of MB removal cycles on the MB desorption percentage.

Although the beads disintegrate with reuse, still the fact that high regeneration percentages were obtained and this defect can be overcome by using lower NaCl concentrations for shorter time. Even the disintegrated beads could be reformulated again and reused.

3.5. Beads characterization

The FTIR spectra of alginate and its IDA functionalized derivative were investigated. Both alginate forms showed a broad band between 3000 and 3800 cm^{-1}, which was attributed to O–H stretching vibrations. The spectrum of alginate showed the peaks at around 2930, 1606, 1417 and 1033 cm^{-1}, indicating the stretching vibrations of aliphatic C–H, COO$^-$ (asymmetric), COO$^-$ (symmetric), and C–O, respectively, which are characteristics of the polysaccharide [18]. As the similar, the spectrum of the alginate-IDA showed the peaks at around 2935, 1625, 1423 and 1033 cm^{-1}, indicating the stretching of aliphatic C–H, COO$^-$ (asymmetric), COO$^-$ (symmetric), and C–O, respectively. Moreover, a new strong bands compared to alginate spectrum at around 1740 cm^{-1} were assigned to carboxylic carbonyl group of IDA, which confirmed the grafting of the IDA (Fig. 9). This is in good agreement with the results reported grafting of carboxylic groups bearing vinyl monomer to different polymeric backbones in the literature [19–22].

Thermogravimetric curves of alginate and IDA activated alginate beads in a nitrogen atmosphere are displayed in Fig. 10. The thermogram of sodium alginate exhibited two distinct stages. One in the range of 30–190 with a maximum decomposition rate at 104°C was assigned to elimination of water adsorbed to the hydrophilic polymer. The other in the range of 210–310°C with a maximum decomposition rate at 248°C was ascribed to a complex process including dehydration of the saccharide rings, depolymerization with the formation of water, CO_2 and CH_4 [23]. The differential thermogravimetric curve of the PBQ activated alginate also showed two identical degradation steps. IDA functionalized alginate beads show different behavior with increase of IDA concentration used in the functionalization process. The losted adsorbed water percentage in first step was reduced along with increase in the IDA concentration. The start of

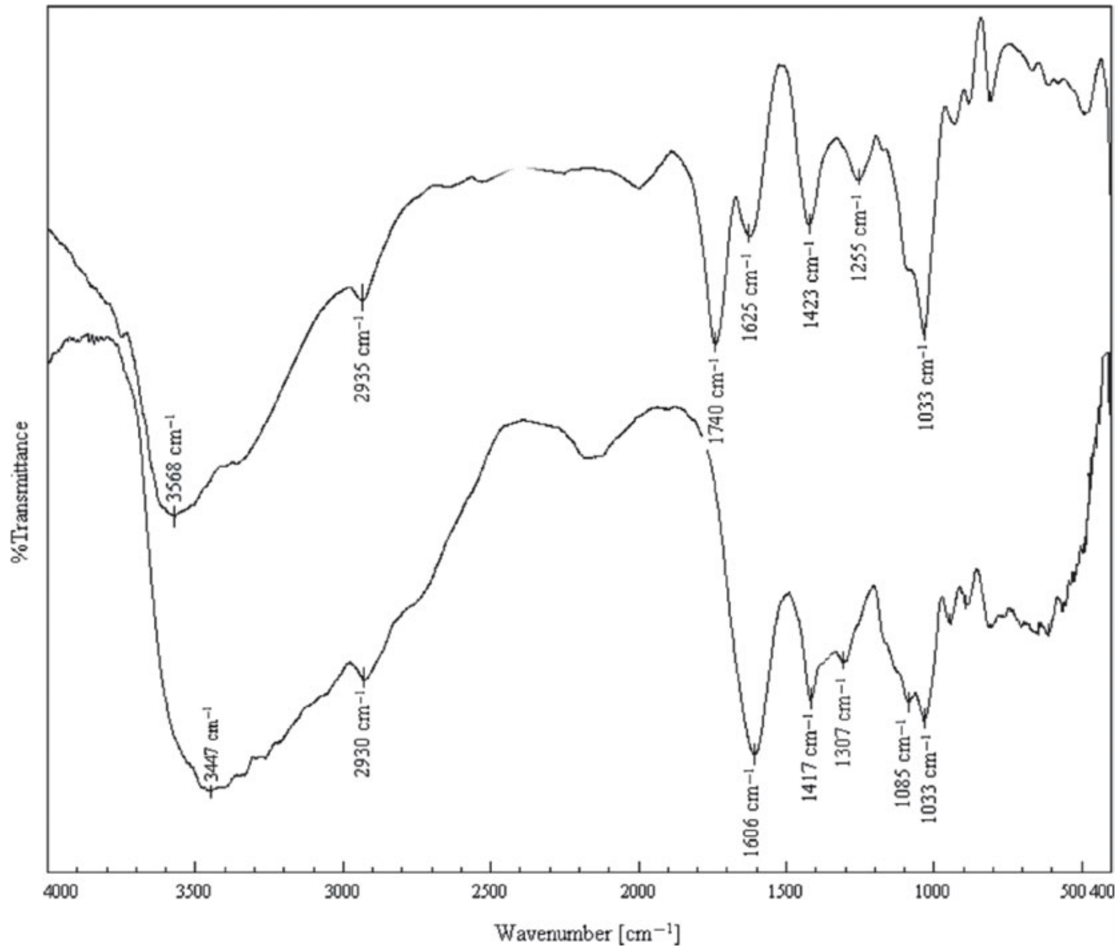


Fig. 9. FT-IR spectrum of alginate (lower curve) and IDA-alginate (upper curve).

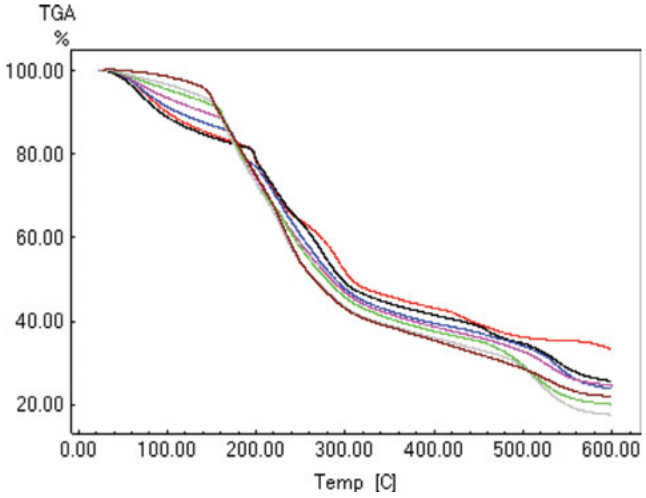
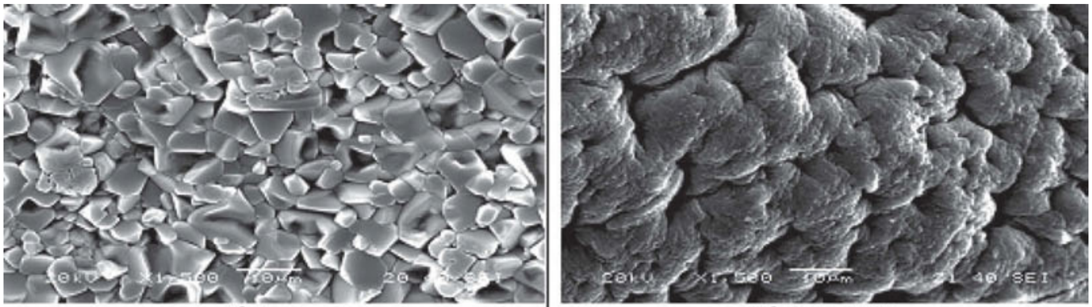


Fig. 10. TGA of alginate (red line), PBQ-alginate (black line), IDA(0.25%)-PBQ-alginate (blue line), IDA(0.50%)-PBQ-alginate (pink line), IDA(1.00%)-PBQ-alginate (green line), IDA(2%)-PBQ-alginate (gray line) and IDA(3.00%)-PBQ-alginate (brown line).

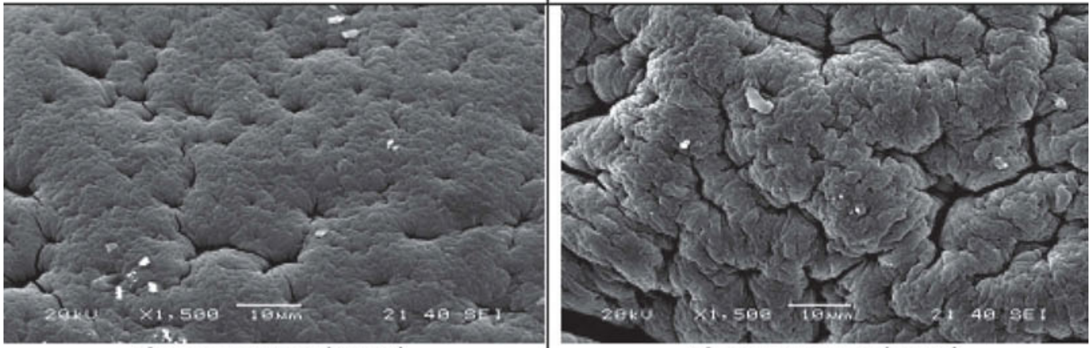
the second stage was gradually shifted to lower temperature along with increase IDA concentration used in the functionalization step to reach 180°C. From the thermal gravimetric analysis (TGA) curves, it can be concluded that the thermal stability of the alginate decreases with the grafting of IDA molecules onto the polysaccharide backbone. This may be attributed to the low thermal stability of IDA as a result of decarboxylation reaction observed second degradation step. This phenomenon has been also reported by Naguib [20]. He has indicated that thermal stability of the polymer reduced with the grafting of IA onto sisal fiber. Nuran Isıklan et al. [24] have obtained the same results with alginate grafted with IA.

The scanning electron micrographs of alginate and IDA functionalized alginate, with different concentrations, are shown in Fig. 11. By comparing the surface morphology we found that the grafted chains of IDA drastically changed the morphology of alginate. As shown in the figure, the surface of the IDA functionalized alginate was more spongy structure than



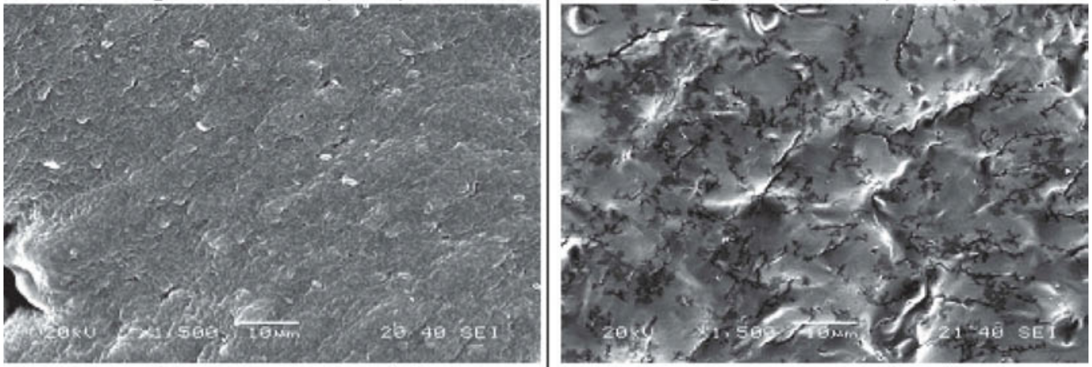
Alginate

Alginate-PBQ



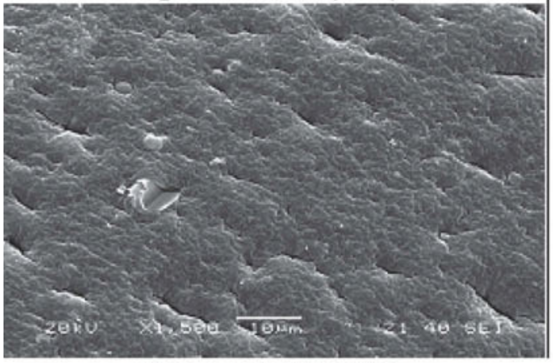
Alginate-PBQ-IDA (0.25%)

Alginate-PBQ-IDA (0.50%)



Alginate-PBQ-IDA (1.0%)

Alginate-PBQ-IDA (2.0%)



Alginate-PBQ-IDA (3.0%)

Fig. 11. SEM photographs of alginate, alginate-PBQ and Alginate-PBQ-IDA beads surface.

that of alginate which may be attributed to the polarity difference between alginate and IDA. At the same time surface of IDA functionalized alginate becoming smoother along with increasing the IDA concentration used in the surface functionalization process. Such behavior was not recognized with PBQ activated alginate beads. This is may be attributed to non polarity nature of PBQ.

4. Conclusions

Surface functionalized alginate beads with carboxylic groups were prepared through activation OH groups with PBQ coupling agent followed by reaction with IDA. The functionalized beads show higher affinity towards MB adsorption compared to native one. A 25% improvement in the dye removal capacity was obtained after 60 min. The functionalized beads show higher adsorption rate for MB. Within 10 min, 80% of MB was removed compared to 48% using functionalized and native beads, respectively. The proposed technique in this work allowed us to have well cross linked beads with better mechanical properties and improved adsorption capacity which enables us from reusing it for several times without concerns about its stability.

References

[1] T. Robinson, G. McMullan, R. Marchant and P. Nigam, Bioresour. Technol., 77 (2001) 247–255.
[2] J.R. Easton, in: P. Cooper (Ed.), Colour in dyehouse effluent, Alden, Oxford, 1995.
[3] B. Chen, C.W. Hui and G. McKay, Langmuir, 17 (2001) 740–747.
[4] C.C. Ribeiro and C.C. Barrias, Biomaterials, 25 (2004) 4363–4373.
[5] O. Smidsrod and G. Skjak-Brk, Trends Biotechnol., 8 (1990) 71–78.
[6] A.K. Pandey and S.D. Pandey, J. Hazard. Mater., 98 (2003) 177–181.
[7] L.K. Jang and D. Nguyen, Water Res., 33 (1999) 2817–2825.
[8] J.H. Min and J.G. Hering, Water Res., 32 (1998) 1544–1552.
[9] M.Y.C. Hyun Gyu Park, J. Chem. Technol. Biotechnol., 79 (2004) 1080–1083.
[10] R.P. Dhakal and K.N. Ghimire, Sep. Purif. Technol., 42 (2005) 219–225.
[11] C. Jeon and J.Y. Park, Biochem. Eng. J., 11 (2002) 159–166.
[12] R. Aravindhan and N.N. Fathima, Colloid Surf. A., 299 (2007) 232–238.
[13] M.F. Nasr and S.M.A. El-Ola, Polym. Plast. Technol. Eng., 45 (2006) 335–340.
[14] V. Rocher, J.-M. Siaugue, V. Cabuil and A. Bee, Water Res., 42 (2008) 1290–1298.
[15] M. Kalman, B. Szajani and L. Boross, Appl. Biochem. Biotechnol., 8 (1983) 515–522.
[16] M. Chun, G. Dickopp and M. Sernetz, J. Sollid Phase Biochem., 5 (1980) 211–221.
[17] I.D. Mall, V.C. Srivastava, G.V.A. Kumar and I.M. Mishra, Colloid Surf. A., 278 (2006) 175–187.
[18] G.M. Patel, C.P. Patel and H.C. Trivedi, Eur. Polym. J., 35 (1999) 201–208.
[19] N. Isıklan, M. Inal and M. Yiğitoğlu, J. Appl. Polym. Sci., 110 (2008) 481–493.
[20] H.F. Naguib, J. Polym. Res., 9 (2002) 207–211.
[21] V. Singh, A. Tiwari, S.P. Singh, P. Kumari and S. Tiwari, J. Appl. Polym. Sci., 110 (2008) 1477–1484.
[22] T. Tripathy and R.P. Singh, J. Appl. Polym. Sci., 81 (2001) 3296–3308.
[23] J. Zhang, Y. Yuan, J. Shen and S. Lin, Eur. Polym. J., 39 (2003) 847–850.
[24] N. Isıklan, F. Kursun and M. Inal, Carbohydr. Polym., 79 (2010) 665–672.