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Rapid and efficient removal of boron from deep sea water using synthesized polymer resin

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ABSTRACT

The present investigation aims to remove boron from deep sea water using the N-methyl D-glucamine-modified polymeric resin as synthesized in the laboratory. The resins are characterized by IR analysis and the morphology is discussed with the help of scanning electron microscopic images. Further, the resin is distributed in three different bead sizes i.e. 0.25, 0.5 and 1.0 mm, and assessed their removal efficiency for the boron removal under batch and column operations. Batch data show that a very fast uptake of boron took place and within 20 min of contact, almost a complete removal of boron occurred. Further, the kinetics of boron uptake is performed using linear equations of pseudo-first-order and pseudo-second-order rate equations. The applicability of pseudo-second-order rate law inferred that the boron is sorbed onto the solid surface by strong chemical forces, forming an "inner sphere complexes". The batch and column data obtained for the boron removal is then critically compared with the commercially available resin. Further, reusability of this resin is also obtained taking the repeated operations using the same used resin. These results may, perhaps, enable to reduce the input cost of deep sea water treatment.

Keywords: Terpolymer; N-methyl D-glucamine; Chelation; Seawater; Boron; Removal

1. Introduction

The increasing demand of water both for potable and irrigation purposes decreases the availability of fresh water resources, which prompted globally to unveil alternative water sources to meet the greater demand of fresh water. The scarcity of water in many regions around the globe is forced to exploit the available seawater sources at some or even enhanced levels [1,2]. However, the use of deep sea water is greatly limited because of significant concentration of boron in sea water. This reported that the boron is an essential micronutrient for the growth and development of plants, humans and animals [3,4]. This possessed structural component of cell walls which is connected with the lignification processes, membrane transport, enzyme interactions, nucleic acid synthesis and carbohydrate metabolism activities [5–7]. This is also important for regulating the hormones in animals [8,9]. However, it becomes toxic once it exceeds a certain level. Moreover, it was reported that the

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presence of boron becomes toxic for plants when the amount of boron is slightly higher than the required. Actually, the difference between the deficiency and excess of boron limit is very less e.g. it is 0.5 and 0.75 for orange, and 4.0 and 6.0 for tomato, respectively [5,6,10]. Additionally, Boron is reported to be toxic for humans and plants. The reproductive dangers are reported with excessive intake of boron in humans. Similarly, it induces premature ripening along with reduced fruit yields as reported, in particular for kiwi fruit [11]. Similarly, a physiological disorder involves with the excess of boron uptake as the reduction of root cell division is retarded, such as shoot and root growth, inhibition of photosynthesis, deposition of lignin and suberin decrease in leaf chlorophyll [5–7]. Based on its toxicity and several adverse effects, the World Health Organization (WHO) has reduced the boron level in drinking water to 0.5 mg/L which is much below to boron contents available in water resources in many areas or even in deep sea water [10]. Boron is usually present in sea water as boric acid, and the deep sea water contains boron ca. 4–5 mg/L. Some of the possible methods are available to remove boron viz., precipitation–coagulation, adsorption, solvent extraction, ultra filtration, reverse osmosis, electrodeionization, ion exchange, membrane technology, etc. [11–13]. Among these, ion-exchange is likely to be promising towards the selective removal of boron from deep sea water. Hence, use of selective and suitable resin [1] is one of the possible methods for efficient removal of boron from deep sea water. The pores of commercially available poly(propylene) membranes are functionalized *in situ* by cross-linking with poly(vinylbenzyl chloride) with a cyclic diamine piperazine. Further, the precursor membranes are chemically modified with N-methyl D-glucamine which is fairly selective towards the boron and shows promising material for selective removal of boron from aqueous solutions [14]. Similarly, polyvinylidene fluoride flat-sheet membrane is utilized in the desalination and boron removal from sea water [15]. Since the boron effectively complexes with the cis-diol group of polysaccharide, therefore, a semi-gel of konjac glucomannan, a polysaccharide, is used in the efficient removal of boron [16].

It is mentioned that three or more hydroxyl functional groups forming a specific complexes with boron esters or borate and materials containing with high density of hydroxyl groups are perhaps effective in boron attenuation from aqueous solutions [17]. Six hydroxyl functional groups containing sugar derivatives, e.g. sorbitol and mannitol, show extremely high boron binding abilities [17]. Moreover, (styrene)-based resin with N-methyl D-glucamine functional groups are proposed for selective and efficient removal of boron [12]. The glycidyl methacrylate (GMA)-based gel polymers with N-methyl D-glucamine functional groups are also useful to remove boron in the form of boric acid [18].

Therefore, keeping in view the high uptake capacity of N-methyl D-glucamine-modified GMA-based gel polymers, the present investigation explores the use of this modified polymer resin for the removal behaviour of boron in deep sea water; also, the efficiency of the polymer is assessed for repeated operations in the batch reactor in order to increase the cost effectiveness. Additionally, the effect of particle size of resin is also studied for the boron removal in batch and column reactor operations using pretreated Ulleung island deep sea water.

2. Materials and methods

2.1. Materials

GMA (Junsei Chemicals, Japan), methylmethacrylate (MMA) (Duksan Chemicals, Korea), divinyl benzene (65% DVB) (Wako, Japan) and N-methyl-D-glucamine (Fluka, China) were procured and used without any further purification. Hydrolyzed sodium salt of maleic acid–styrene copolymer (STMA) (Aldrich, Germany), azo-bis-isobutyronitrile (AIBN) (Junsei Chemicals, Japan), N-methyl pyrrolidone (Junsei, Japan) and other chemicals were used of analytical or equivalent grade chemicals. The commercial resin was obtained from the Nihonkaisui Co. Ltd, Japan. The deep sea water was collected from Ulleung island near Korean Sea and was further pretreated with membrane filter 50 GPD (Clean one, USA) by the private company Gangneung IND, Korea, as to remove the salt contents from the sea water. The pretreated sea water was having the boron concentration of 4.604 mg/L as detected by the inductively coupled plasma mass spectrometer (ICP-MS, DRC-11 Perkin Elmer) (USA). The pretreated sea water was then used for this investigation.

2.2. Synthesis of resin

The GMA–MMA–DVB terpolymer resins bead was synthesized with the known method as given elsewhere [19]. In brief, 4 g Na_2SO_4 was dissolved in 5.75 mL hydrolyzed STMA in a three-necked round bottom flask and then 300 mL water was added under continuous stirring in nitrogen atmosphere as N_2 gas was bubbled slowly into the solution mixture. In an another flask, 26.4 mL GMA and 26.5 MMA with 10.03 g DVB and 1 g AIBN was dissolved in 60 mL of toluene. This solution mixture was added dropwise (ca. 30 min) to the previously obtained hydrolyzed STMA solution, and was further stirred ca. 10 h with 400–500 rev/min at room temperature and under N_2 atmosphere. The solution was then poured into 1 L of cold distilled water. Spherical beads of GMA–MMA–DVB terpolymer resins were suspended in this water. These beads were washed with excess of water followed by 50 mL of ethanol, dried under vacuum for 24 h and stored in an airtight polyethylene bottle. The yield of the resin was ca. 50.0 g and it contained varied bead sizes 1–0.125 mm. Moreover, it also contained some unreacted DVB, which was simply taken out manually since these were aggregated relatively as a big aggregate in the dried resin.

2.3. Modification of resin beads

For improving the adsorption capacity of solids for boron, additional hydroxyl groups were introduced within the polymer resin as this was modified with the N-methyl D-glucamine. N-methyl D-glucamine (15.0 g) was dissolved into 110 mL of N-methyl pyrrolidone by heating under stirring at 80˚C placed in a silicone oil bath. Previously prepared GMA–MMA–DVB terpolymer resin of 17.1 g was then added, in portions, into the hot solution. Reaction was stirred continuously under reflux for 4 h at 80˚C. The mixture was cooled and poured into 1 L of cold water. The resin was simply decanted and the supernatant (almost white in colour) was thrown out followed by filtration using GF/C filter paper. The beads were washed with excess of water followed by 50 mL of methanol. These beads were dried under vacuum (ULVACC SINKU KIKU, VPC-260) over night at room temperature and stored in an airtight polyethylene bottle. The yield of the modified resin was ca. 20.2 g. The morphology of beads was carried out by scanning the resin particles using a scanning electron microscope (SEM) (Nanoeye, Korea; Model No. SNE-1500 m) and structural determination was carried out by FT-IR (Bruker).

2.4. Boron adsorption by batch method

It was observed that resin prepared by this method contained various bead sizes ranging from 0.125 to 1.0 mm of size. Hence, three different bead sizes i.e. 0.25, 0.5 and 1.0 mm were collected using the BS standard sieves. The removal of boron was performed by taking 50 mL of pretreated deep sea water (4.604 mg/L) equilibrated with 0.5 g of resin separately for three different samples of resins having different bead sizes. The solution mixture was stirred at room temperature manually and the aliquots were collected at certain time intervals i.e. 5, 10, 15 and 20 min of contact. The bulk boron concentration was checked by the ICP-MS (DRC-11 Perkin Elmer, USA).

2.5. Boron adsorption by column method

Further, the suitability of this resin (having different bead sizes) was examined under the dynamic conditions i.e. under the column experiments. While performing the column studies, the identical conditions were maintained i.e. the same resin dose and same boron concentration with same sorptive volume 50.0 mL. Resin beads of 0.5 g were loaded in a column (1 cm diameter) and the sorptive boron solution was pumped upward through the column with the controlled flow rate of 1.2 mL/min, and the 50 mL of effluent solution was collected in a beaker. The bulk boron concentration of the effluent water along with the influent solution was checked by ICP-MS.

3. Results and discussion

3.1. Morphology and characterization of resin

The SEM image obtained for the synthesized resin is shown in Fig. 1. This clearly shows that the resin shape is almost spherical and small in size (ca. 308 μm), and no micro- or mesopores were opened/located on its surface. This inferred that the hydroxyl functional groups were predominantly present on the resin beads that may bind the boric acid specifically by forming either neutral boron ester or borate complex anion with a proton as counter ion [17,19].

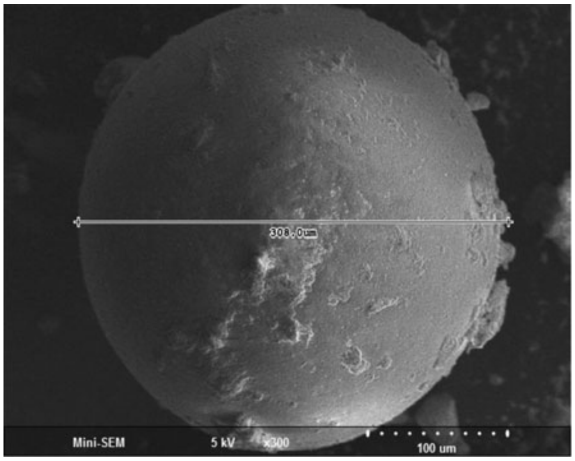

Fig. 1. SEM image of the N-methyl D-glucamine-modified resin.

Further, the FTIR spectra of unmodified resins along with modified resins were obtained and shown in Fig. 2(a) and (b), respectively. Both spectra were not differed markedly with each other and only the broad bands occurred at the frequency 1,150 and 3,300–3,500 cm^{-1} with modified resin. The band at 1,150 cm^{-1} was due to the five carbinols of the NMG function of the resin, and a pronounced broad peak at 3,300–3,500 cm^{-1} indicated –OH stretching vibrations in the structure of the modified resin. The modification of resin was gained with additional hydroxyl groups with enhanced hydrophilicity and volume expansion in water substrate which enables it an effective material for specific boron complexation.

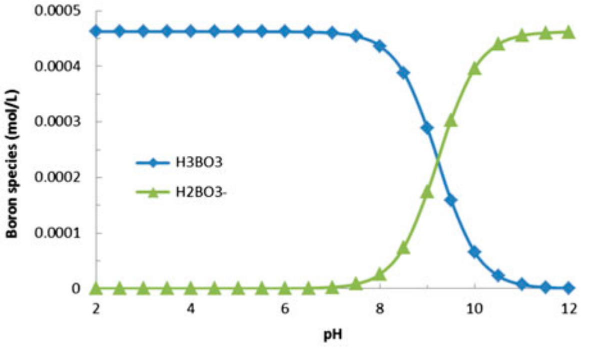

Fig. 3. Speciation studies of boron in aqueous solutions as a function of pH.

3.2. *Adsorption by batch method*

The speciation study of boron in aqueous solution is carried out using the Visual-MITEQ speciation computer simulation program at the initial concentration of 5.0 mg/L, and the results obtained are presented in Fig. 3. The figure clearly demonstrates that at pH around 6.5, the dominant species of boron is only H_3BO_3. Therefore, this is the species only involved in the complexation process by the applied resins. The boron concentration of the pretreated Ulleung island sea water is found to be 4.604 mg/L. Further, these pretreated sea water is subjected for the boron removal using three different sized resins in batch experiments and the batch data obtained is shown graphically in Fig. 4. Fig. 4 clearly shows that the resin possessed significant high affinity towards the boron and within initial 10 min of contact, most of the boron is removed from the aqueous solution, and after 20 min of contact almost 99% of boron is removed leaving very insignificant amount of boron in the bulk solution. Further, this figure also demonstrates that decreasing the bead size from 1.0 to 0.25 mm greatly enhances the rate of uptake of boron from aqueous solutions. This increased uptake rate of boron with relatively lower bead size resin could be explained with the fact that more and more active sites are available with decreasing the bead size. Moreover, the treated samples contain only 0.192, 0.125 and 0.025 mg/L of

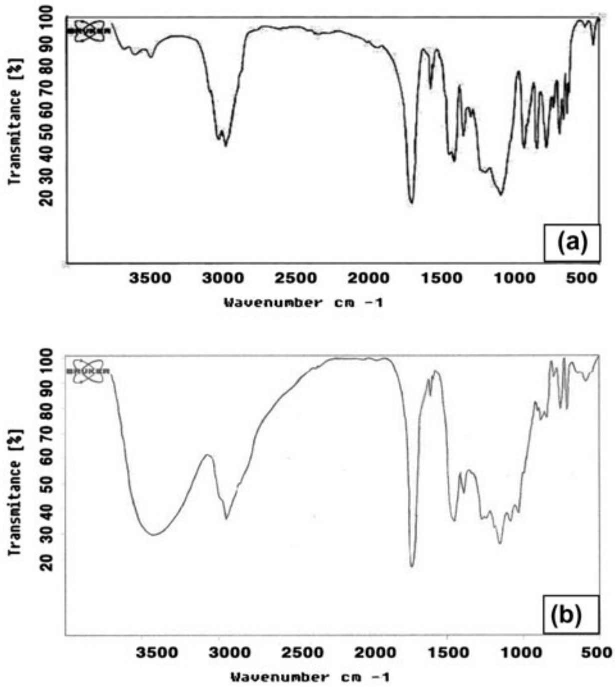

Fig. 2. FTIR spectra of (a) resin and (b) N-methyl D-glucamine-modified resin.

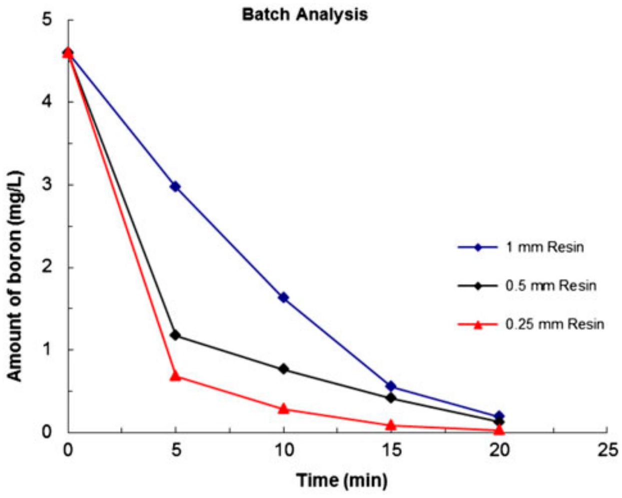

Fig. 4. Removal behaviour of N-methyl D-glucamine-modified resin for boron as a function of resin bead size and time of contact.

boron in bulk deep sea water, respectively, for 1.0, 0.5 and 0.25 mm of bead sized resin; these values are significantly less than the WHO prescribed value of 0.5 mg/L of boron for the drinking and even irrigation use of water. Hence, the resin shows very efficient and rapid removal behaviour particularly in the removal of boron from deep sea water.

3.3. Comparative study

In order to compare the boron sorption capacity of synthesized resin with the commercially obtained resin under the identical batch experimental conditions, experiments are performed for the removal of boron from aqueous solutions at constant pH of 6.5. The results obtained with batch experiments are shown graphically in Fig. 5, which clearly demonstrates that the synthesized resin even with higher bead size possess very high boron removal capacity comparing to the commercial resin. More precisely, up until 20 min of contact, only 0.69 mg/L of boron is removed or only 16% of boron removal is occurred by commercial resin comparing to 1 mm sized resin, which could remove more than 95% of boron for the similar experimental conditions. Similarly, on the other hand, the column data (which is shown in cf. Fig. 7 and discussed elsewhere in Section 3.4) also demonstrates that the synthesized resin with three different bead sizes i.e. 0.25, 0.5 and 1.0 mm possessed significantly higher removal capacity comparing to the commercial resin. Hence, these data clearly inferred that the synthesized resin with all available bead sizes shows significantly higher removal efficiency/capacity towards the boron comparing to the commercial resin. Hence, this could have potential alternative for the treatment of deep sea water either for the irrigation or potable water purposes.

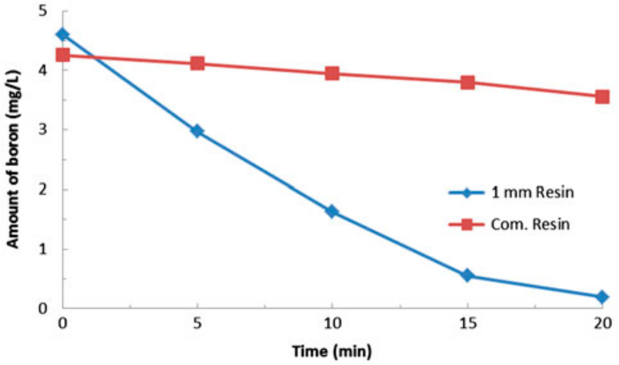

Fig. 5. Comparable removal behaviour of commercial and 1 mm bead sized resin for boron in deep sea water.

Further, the kinetic study was performed for the Lagergren's pseudo-first-order rate and pseudo-second-order rate equations employed in its linear form as given in Eqs. (1) and (2) [20,21]:

$$\text{Log}\,(q_e - q_t) = \text{Log}\,q_e - k_1 \times \frac{t}{2.303} \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_0^2} + \frac{1}{q_0 \cdot t} \tag{2}$$

where q_e and q_t are the amount of boron sorbed at equilibrium and at time "t", respectively. q_0 is the maximum sorption capacity of boron by the modified resin. k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants, respectively. The plots were drawn between the Log $(q_e - q_t)$ vs. "t" and t/q_t vs. "$1/t$", respectively, for the pseudo-first-order and pseudo-second-order rate laws, respectively. The validity of these models is much based on the values of correlation coefficient, R^2. Further, the values of rate constants (k_1 and k_2), q_e and q_0 along with the R^2 values are estimated based on the fitting of data with Eqs. (1) and (2), and then returned in Table 1 for the systems studied. It is observed that the uptake of boron by these solids followed the pseudo-second-order rate equation fairly well comparing to the pseudo-first-order rate equation, since the R^2 values are extremely high for pseudo-second-order rate kinetics. It is worth to be pointed that the applicability of pseudo-second-order kinetic model in the sorption of boron by these resins indicates that "chemisorption" is a predominant process involved with valency forces through sharing or exchange of electrons between the sorbent and the sorbate ions [22–24]. Moreover, the value of q_0 estimated for these solids for boron clearly shows that the N-methyl D-glucamine-modified resin possessed significantly higher removal capacity than commercial resin.

3.4. Adsorption by the column method

Further, the removal behaviour of these resins are assessed under the dynamic conditions i.e. the column experimentation. Results obtained are shown in Fig. 6. These results are obtained with identical conditions to the batch experiments i.e. same initial resin dose, 0.5 g, and the total eluted volume was 50 mL through the column with the controlled flow rate of 1.2 mL/min. Results clearly show that the removal of boron is dependent to the bead size of the resin. By decreasing the bead size 1–0.25 mm, the amount of boron removal is increased 3.425–4.155 mg/L with the initial boron concentration of 4.254 mg/L. These results are quite in

Table 1
Kinetic simulation results for the sorption of boron by different resin samples

	Pseudo-first order			Pseudo-second order		
Systems	k_1	q_e	R^2	k_2	q_0	R^2
1.0 mm resin	0.2045	0.8720	0.959	66.88	0.1222	0.992
0.5 mm resin	0.1297	0.2105	0.983	10.17	0.3136	0.999
0.25 mm resin	0.2418	0.2410	0.983	7.47	0.3658	0.999
Com. resin	0.0843	0.865	0.994	9,583.25	0.0102	0.987

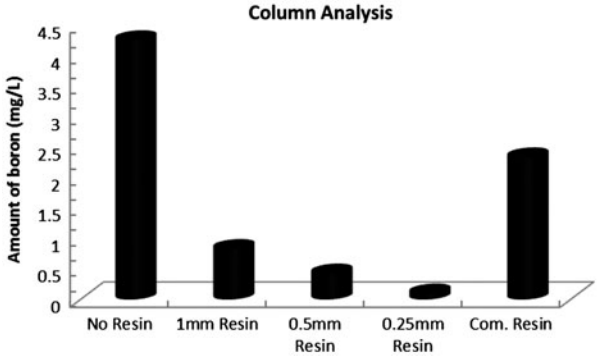

Fig. 6. Removal behaviour of different resins for boron under column experiments.

a line to the batch data. Moreover, results further indicate that N-methyl D-glucamine-modified resin could be a potential material to be employed for its wider implication in the treatment of deep sea water particularly for the boron removal.

3.5. Reusability of the resin beads

One of important characteristic of this co-polymer-based resin bead is its reusability. Hence, in terms of cost effectiveness, the resin is used for the repeated cycle operation in batch experiments and the results obtained are shown in Fig. 7. The initial boron concentration is 4.254 mg/L, and the 0.25 mm-sized resin is used as a reference material. Fig. 7 clearly demonstrates that even after six recycles of resin applications, it removes more than 93% of boron i.e. 0.298 mg/L of boron left in the bulk solution. Hence, resin could possess very high removal capacity and can be employed for successive operations of boron treatment. Further, in order to optimize the maximum number of recycling which can be done to obtain the maximum of 1.0 mg/L of bulk boron concentration (i.e. Korean standard of drinking water). A plot has been drawn between the number of recycling and the bulk boron concentration (cf. Fig. 8); reasonably a good straight line is obtained with the slope of 0.0508. Hence, with this linear relationship, it is calculated that the resin

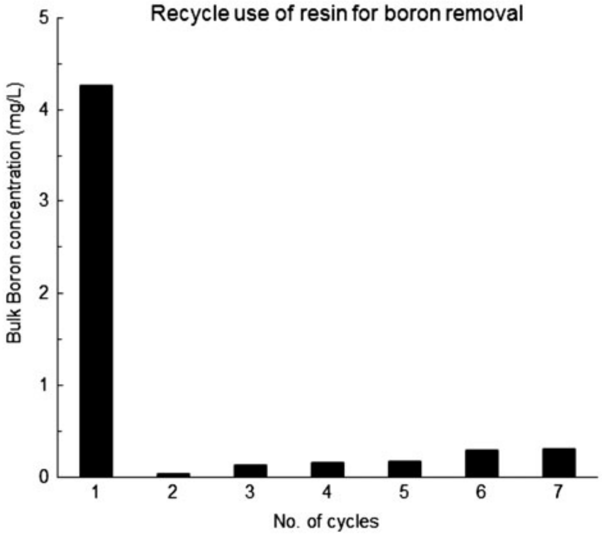

Fig. 7. The recycle use of resin for boron removal in batch experiments: (1) initial boron concentration, (2) first, (3) second, (4) third, (5) fourth, (6) fifth and (7) sixth cycle use of resin beads (0.25 mm size).

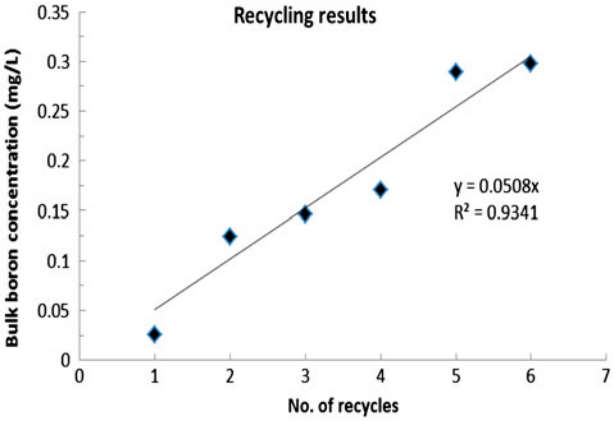

Fig. 8. The relationship of recycling with the bulk boron concentration.

may be used for ca. 19 times as to obtain the bulk boron concentration of 1.0 mg/L. In other words, 0.5 g resin can be employed for the treatment of ca. 950 mL of deep sea water containing 4.254 mg/L of boron. These results clearly show that the N-methyl D-glucamine-modified resin possessed significantly a high removal capacity for the boron and likely to be cost effective effectiveness.

4. Conclusions

The N-methyl D-glucamine-modified resin was synthesized in the laboratory and the morphology of resin beads showed that good spherical type of beads occurred with an average bead size of 308 μm. The IR data showed that carbinols and hydroxyl groups were present within the resin structure. Further, the resin was distributed in three different sizes i.e. 0.25, 0.5 and 1.0 mm and employed to assess the removal behaviour for boron in deep sea water. Batch data showed that within 20 min of contact, ca. 95% of boron was removed and with decreasing the bead size, the uptake of boron was increased and reached to 99% with 0.25 mm bead-sized resin. On the other hand, keeping identical experimental conditions as with batch experiments, the column data also demonstrated that almost 98% of boron was removed. Similarly, the removal capacity was increased with decreasing the bead size. The kinetics of boron uptake was assessed using the pseudo-first-order and pseudo-second-order rate equation which demonstrated that the uptake of boron by these resins followed pseudo-second-order rate law. This further indicated that the boron is sorbed by the strong chemical forces, forming an “inner-sphere-complexes” onto the resin surface. Further, the reusability of these solids were also estimated with repeated operations using the used resins, and it was observed that even after the six recycle of the resin, it possessed remarkably high removal efficiency/capacity as it can remove more than 93% of boron in deep sea water. Additionally, the resin was compared with one commercial resin in batch experiments which indicated that the synthesized resin possessed with significantly high removal capacity over commercial resin. Hence, the resin could be a potential, and perhaps cost effective, alternative for the treatment of deep sea water.

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