



Research Article

Boron removal from aqueous solutions by polyethyleneimine- Fe³⁺ attached column adsorbents

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ABSTRACT

Although, boron (B) is an essential micronutrient for plants, animals and human beings; at high concentration of boron in water resources may be hazardous for living being. Hence the boron concentration has to be reduced down to suggested level by the World Health Organization for safe use of water for irrigation and drinking. The present study examines boron pollution level in groundwater and suggests an alternative sorbent to remove it from water sources used for irrigation and drinking. The poly-2-Hydroxyethyl methacrylate (HEMA)-co- glycidyl methacrylate (GMA)- polyethyleneimine (PEI)- Fe³⁺ columns were synthesized to adsorb the boron compounds from a real groundwater samples and synthetic solution. Boron was removed 78.2% by poly (HEMA-co-GMA)-PEI- Fe³⁺ column at an amount of 54.42 mg/g, pH 8. However, the lower adsorption ratio was recorded as between 35.8–58.1% of real groundwater where adsorbed amount of boron and its derivatives were found as 9–28.67 mg/g due to other chemical ions in real groundwater samples. Boron-loaded columns were regenerated by 0.01 M NaOH treatment for industrial practice. Regeneration cycles were performed successfully 15-times with only a loss of 5% in adsorption capacity of columns.

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INTRODUCTION

Water scarcity has been recognized as an important issue for agricultural production. Many freshwater resources have been reported to be suffering from overexploitation and misuse [1]. This outcome has increased dependency on groundwater resources being used for irrigation. Hence it is fundamental issue to ensure the quality of groundwater where it used for public and domestic supply Boron and its derivatives common in groundwater sources along with other constituents from the areas with volcanic geology [2].

Boron (B) presents in the lithosphere of the earth and it is mostly found in the form of boric acid and borate salts in the environment [3, 4]. Boron becomes harmful to plants and animals when its amount is greater than required for growth [5]. In fact, boron has been recently re-established as a contaminant in various water supplies due to its industrial use, mainly to produce fiberglass, fertilizers, detergent, ceramic, glass etc. [6]. Water-soluble boron is available in the form of boric acid (H₃BO₃), borates, and anionic polyborates including [B₃O₃(OH)₄]⁻, [B₄O₅(OH)₄]⁻², [B₅O₆(OH)₄]⁻ [7]. Excess

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amount of boron is toxic for plants causing various adverse effects including edge and tip necrosis, loss of pigmentation in the leaves, problems in root cells, weaker photosynthesis, etc.

The World Health Organization (WHO) regulated a boron standard less than 2.4 mg/L for drinking water and 1 mg/L or less for irrigation [8] in fact it is 0.5 mg/L due to the herbicidal effect of boron [9]. However, EU Drinking Water Directive and Environmental Protection Agency (EPA) regulated the boron concentration in drinking water to 1.0 mg L⁻¹ [10, 11]. The largest boron producers in the world are Turkey and The United States, hence these countries have the most significant boron contamination problems [12]. Some parts of Turkey, especially the areas of Bursa-M. Kemalpaşa-Kestelek, Balıkesir-Bigadiç, Kütahya-Emet and Eskişehir-Kırka are naturally high in boron mineral. Turkey has 70% of the total boron reserve of the world. The USA has the second biggest reserve, which is 13% of the world [13, 14].

There are many techniques to remove boron from aqueous environment including precipitation-coagulation, reverse osmosis, electrodialysis, membrane filtration, ultrafiltration and adsorption [1, 15–19]. On the other hand, alternative adsorbents for removing boron from aqueous environments have been receiving worldwide attention for to prevent from occurring breakdown products of conventional methods. Especially, polymer, membrane-based separations have received great attention owing to their efficiency in the consumption of energy, cost and their possibility in regeneration [20–22]. Polymer or silica supported poly-hydroxyl molecules, such as N-methyl-D-glucamine [23] have been widely used as boron-specific adsorbent [19].

Wolska and colleagues [24] have produced monomer mixtures modified with N-methyl-D-glucamine. Their polymer had a good performance adsorbing boron from both acidic and basic solutions. In another study, a novel adsorbent of silica-supported N-methyl-D-glucamine polymers were synthesized by attaching the trimethoxysilane [25]. Boron removal from neutral water was studied with epoxy-amine cross-linked poly(glycidyl glycidyl ether) (PGGE) membrane and linked with N-methyl-D-glucamine (NMDG). The boron removal rate was found better than commercial boron selective resin [26]. Another, glycidol-functionalized macroporous polymer with different amounts of amino and imino groups was subjected for boron removal. The maximum adsorption was recorded 29.22 mg/g with the presence of some ions [27]. The poly-2-Hydroxyethyl methacrylate-co-glycidyl methacrylate - polyethyleneimine- Fe³⁺ (Poly -HEMA-co-GMA-PEI-- Fe³⁺) columns was investigated for arsenic and other metals' reduction previously to this study with a success of removal rate of 71.3–95.4% and 43.2–99.7% respectively [2].

The objective of this study was to examine boron adsorption capacity of the polymers from aqueous environment. For this aim, the synthetic aqueous boron and real groundwater samples, which have been used for drinking and irrigation were tested with poly (HEMA-co-GMA)-PEI-- Fe³⁺ columns. The columns proved to be having good performance to remove arsenic species in our previous study. Structure of the polymer were analysed by scanning electron microscopy (SEM) and Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR). Tests were carried out by a Spectro Genesis Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-QES).

MATERIALS AND METHODS

Materials

Synthetic solution of boron was prepared by dissolving ACS grade H₃BO₃ in Mili Q deionized water (Milipore Sigma) and the ground water samples were collected from 4 wells where water is used for drinking and irrigation purposes in Aksaray provinces. Groundwater was containing various chemicals besides boron species such as Al³⁺, Ba²⁺, Li⁺, F⁻, Cl⁻, Br⁻, NO₃⁻, N PO₄⁻³, SO₄⁻², Ca²⁺, Na⁺, K⁺, Mg²⁺, Si, V and As.

Chemicals, including 2-Hydroxyethylmethacrylate (HEMA), N,N'-methylene-bis-acrylamide (MBAAm), glycidyl methacrylate (GMA), ammonium persulfate (APS), polyethyleneimine (PEI) and H₃BO were purchased from Sigma - Aldrich (St. Louis, MO USA). N,N,N',N'-tetramethylethylene-diamine (TEMED) were supplied from Fluka AG (Buchs, Switzerland). Other chemicals were provided by Merck AG (Darmstadt, Germany).

Characterization of Polymeric Cryogel Sample

Free water volume in Fe³⁺-PEI polymer sample was calculated for the porosity, and shown with ϕ . A piece of polymeric cryogel sample was immersed in the water for swelling. Then, this swelled cryogel sample was put into deionized water having V_1 volume. Later, changed volume (total volume) was marked as V_2 . Finally, difference between two volumes was computed as following equation:

$$V_0 = V_2 - V_1 \quad (1)$$

While the swelled polymeric cryogel sample was weighed as m_w , this sample was pressed by hand, and weighed again as m_s . The obtained weights were used to determine the porosity (ϕ). Here, " ρ_w " symbol was used for deionized water density (Eq. 2).

$$\phi = (m_w - m_s) / \rho_w \times V_0 \times 100 \quad (2)$$

After this process, squeezed polymeric cryogel sample was put in the oven (60 °C, 12–24 h) for obtaining completely dried cryogel and symbolized as " m_d " for calculation total water fraction (TWF) (Eq. 3)

$$TWF = (m_w - m_d) / \rho_w \times V_0 \times 100 \quad (3)$$

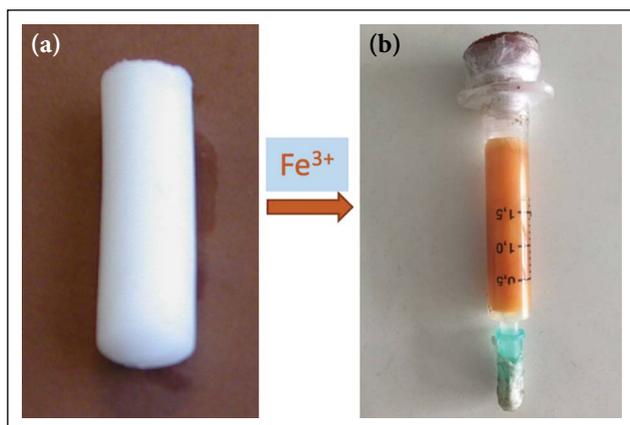


Figure 1. Polymer column (a) and Fe³⁺-attached poly (HEMA-co-GMA)-PEI column (b).

Preparation of poly (HEMA-co-GMA)-PEI

A solution of *N,N*-methylene-bis-acrylamide (MBAAm) prepared with 40 mg of it, in 2 mL of deionized water. Then the solution was mixed with 0.350 mL of 2-Hydroxyethyl methacrylate (HEMA) monomer. Glycidyl methacrylate (GMA) (0.04 mL) used as co-monomer was added to this solution, then the mixture was taken into to a plastic syringe and exposed to nitrogen gas for about 2 minutes to cast out the dissolved oxygen. 100 μL (10% (w/v) of ammonium persulfate (APS) and 20 μL of *N,N,N,N*-tetramethylethylene-diamine (TEMED) were added to final mixture and the mixture was situated at -14 °C for 24 h into a deep freezer. Eventually, the synthesized poly (HEMA-co-GMA) was thawed at room temperature to obtain poly (HEMA-co-GMA) cryogel column. Then the column was washed with Mili Q water-ethanol mixture to remove different impurities such as non-polymerised monomers, initiators (APS) and catalyzer (TEMED).

After obtaining poly (HEMA-co-GMA) cryogel column, PEI molecules were immobilized to it via reactive glycidyl groups on GMA. Because of viscous media of GMA, initially a solution of 30 mL of it (10%, w/v, pH 10.6) was prepared, and synthesized poly (HEMA-co-GMA) cryogels were immersed to this solution through 4 hours for reaction of reactive groups between GMA and PEI (50 °C, 100 rpm). After the reaction was completed, PEI anchored poly (HEMA-co-GMA) polymers were washed with deionized water repeatedly to remove the unreacted and physically adsorbed PEI molecules (Fig. 1).

Fe³⁺-Attachment to Poly (HEMA-co-GMA)-PEI

Attachment of Fe³⁺ ions to poly (HEMA-co-GMA)-PEI cryogels was performed in a solution containing 50 mg/mL of Fe(NO₃)₃ at pH 4.0–4.5 adjusted with 0.01 M HNO₃ (at 25 °C, for 2 h). they were washed several times to remove unbounded Fe³⁺ ions until no Fe³⁺ was detected in washing solution. The leakage of Fe³⁺ ions was checked at initial, and final washing solutions by graphite furnace atomic absorption

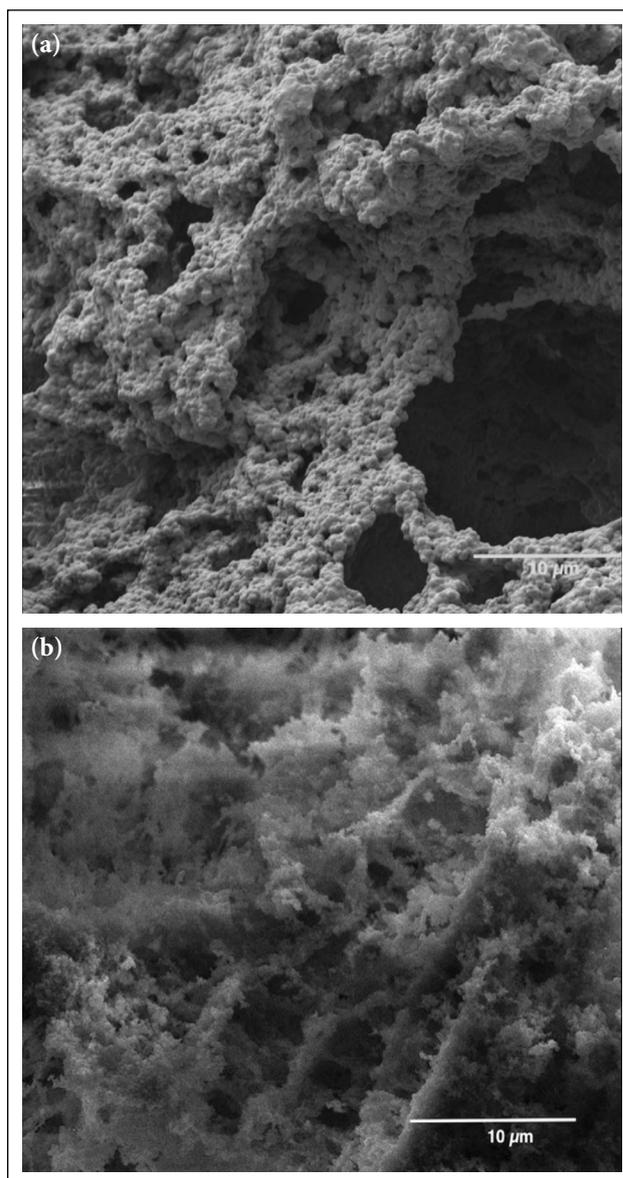


Figure 2. SEM images of the poly (HEMA-co-GMA) (a) and poly (HEMA-co-GMA)-PEI (b).

spectrometer (GFAAS, Analyst 800/ PerkinElmer, USA). Ion solutions are diluted to certain rates before analysing.

SEM Analysis

The morphology of the polymer was studied by scanning electron microscopy (SEM), (EVO LS 10 ZEISS 5600 SEM, Tokyo, Japan). The procedure was for SEM examination earlier described in Baran et al. [15]. Basically, water-swelled polymers were treated in 98% ethanol for exchanging of alcohol molecules with water ones in structures, and the columns were taken to a vacuum oven to extract alcohol from the columns at 50 °C. After dehydration, dried columns were coated with gold-palladium (40:60 nm) and examined for SEM (Fig. 2). Coating was done with sputter coater under vacuum.

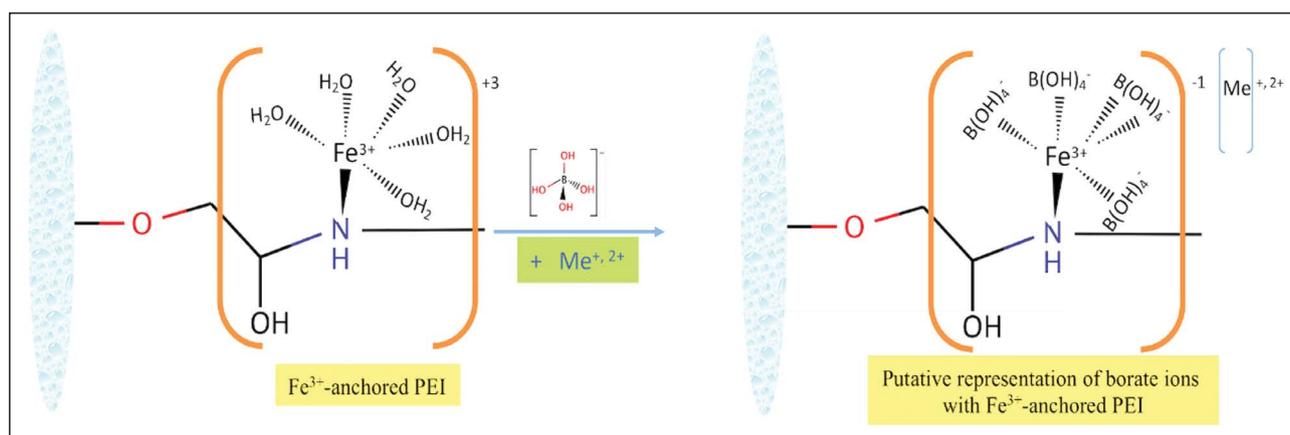


Figure 3. The putative representation of boron derivatives adsorption on Fe^{3+} -PEI polymer (Me represents $^{+1}$, $^{+2}$ valance ions in solution).

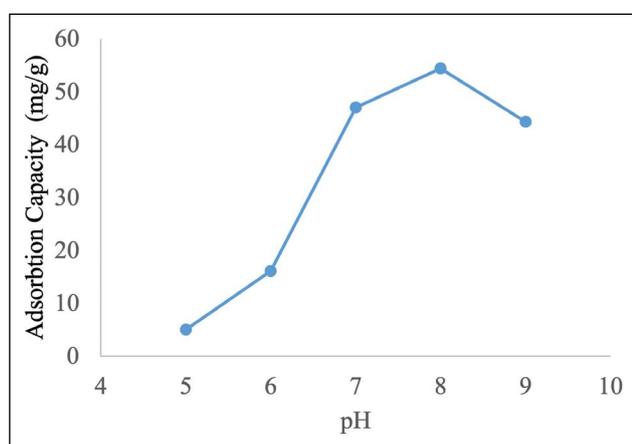


Figure 4. Effect of pH on adsorption of boron derivatives onto poly (HEMA-co-GMA)-PEI- Fe^{3+} composite column.

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectrum of PEI Figure 6 taken with a Mattson FTIR spectrophotometer in the $4000\text{--}400\text{ cm}^{-1}$ range where 30 scans were recorded at 4 cm^{-1} resolutions for solid sample.

Boron Adsorption Studies

Boron adsorption was examined by Fe^{3+} -polyethyleneimine (PEI) anchored-poly (hydroxyethyl methacrylate-co-glycidyl methacrylate) column (poly(HEMA-co-GMA)-PEI- Fe^{3+}) which prepared according to the of Gürbüz et al. [2].

Plastic columns of 0.5 cm internal diameter and 12 cm length with polymeric cryogels (0.1g dried weight) were used in the tests. Removal of boron and groundwater chemicals were either given as mg/g sorbent (Eq. 1) and percentage (Eq. 2), respectively.

$$Q = [(C_o - C_f)V]/m \quad (1)$$

$$\%Q = [(C_o - C_f)/C_o] \times 100 \quad (2)$$

Where Q (mg/g), is the amount of adsorbed boron derivatives (i.e., Boric acid, Borate ions), C_o (mg/L) is the initial concentration, C_f (mg/L) is the remaining boron in solution at equilibrium. V (L) is the volume of the solution; m (g), is the mass of sorbent used in adsorption.

The effect of pH (5–9) was tested with 40 mg/L synthetic boron solution, The effect of initial concentration was tested (2, 4, 10, 15, 40, 50 mg/L). The volume was 200 ml for the carried-out tests.

Natural groundwater samples with various chemicals from 4 well were obtained and put into test with the polymeric cryogels Groundwater was containing various chemicals besides boron species such as Al^{+3} , Ba^{+2} , Li^{+1} , F , Cl , Br , $\text{NO}_3\text{-N}$, PO_4^{-3} , SO_4^{-2} , Ca^{+2} , Na^{+1} , K^{+1} , Mg^{+2} , Si , V , As .

Boron level were recorded via an Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Optima 2100 DV, Perkin Elmer). Analyses were carried out prior to column tests and afterwards.

The putative representation of removal boron derivatives has been schematically presented in Figure 3.

Desorption of Adsorbent

After boron adsorption the polymeric cryogel columns were eluted with MilliQ water three times and then treated with 5 mL 0.01 M NaOH as stripping agent. Regeneration of polymeric cryogels was given in our previous study [2].

RESULTS AND DISCUSSIONS

Characterization of polymeric cryogel sample

The porosity measurement, ϕ , and the total water content, TWC, for Fe^{3+} -PEI polymeric cryogel were computed as 71.8% and 91.5% (v/v), respectively. These results revealed that small pores of Fe^{3+} -PEI polymeric cryogel have bound 19.7% of the total water while flowing liquid was not passing through the Fe^{3+} -PEI polymeric cryogel. The large

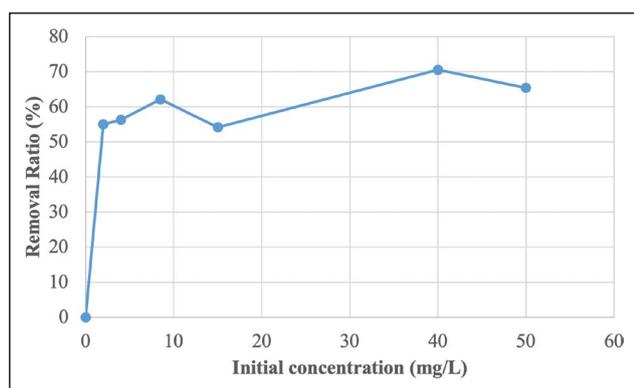


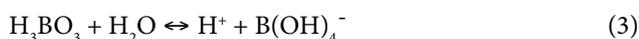
Figure 5. The effect of initial concentration of boron on % of removal ratio at pH 8.

pores wherein the liquid following paths were occurred and formed 71.8% of the total pores, were filled with free water.

The amount of chelated Fe³⁺ ions on PEI polymeric cryogel was found as 2.11 mg Fe³⁺ ions/g polymer.

Boron Removal as a Function of Solution pH

Boron in nature, mainly occurs in boric acid (B(OH)₃ or H₃BO₃) forms and its salts (borates) or as boro-silicates [28]. Molecular boric acid (H₃BO₃) usually appears at low pHs, and performs as an electron acceptor agent in water, whereas at higher pHs the anionic form (metaborate) of boron is predominant (Eq. 3) The reaction of boric acid in aqueous environment expressed in Eq. 3.



Boric acid ratio at near neutral pHs in dilute solutions is found more than 99% [19]. The effect of pH was examined with initial boron concentration of 40 mg/L and in the pH range from 5 to 9. The working volume was 200 ml (Fig. 4). The equilibrium total boron adsorption capacity (Q) of the polymer columns increased with the increase of pH in the range of 5–8 and was maximum at pH 8 (54.42 mg/g). The adsorption of boron species above pH 8 was further indicated by a decrease through the columns (Fig. 4). Similarly, the maximum efficiency of boron removal was reported to be at the initial pH of 8 [29, 30].

In another study, the maximum sorption capacity of boron was observed at pH 9.0 as 55 mg/g; however, it decreased over pH 9.5 [18]. The acid dissociation constant (pKa) of boric acid shows diversity between 8.6–9.2 regarding medium salinity [31]. hence in solutions of pH 9.0, the divalent anion H₁₀(BO₃)₄²⁻ is the predominant species, while in those of pH 8.0 and 10.0 the ratio of bivalent/monovalent anions is close to unity [32]. In the present study, the higher adsorption of the polymer in boron removal from water at pH 8 can be related to the change of the electric charge of boron and Fe³⁺ ions at different pHs. At lower pHs, boron often appears in the form of boric acid, and at higher pHs, it is usually in the

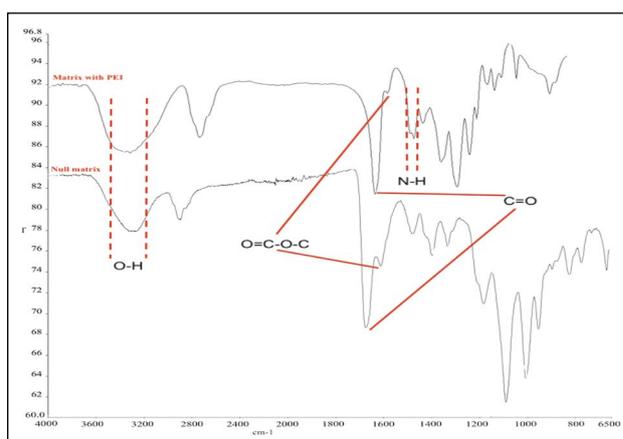


Figure 6. FTIR spectra of matrices with PEI and without PEI molecule.

Table 1. Boron/boron derivatives removal by the Fe³⁺-PEI polymeric cryogel column

Samples	pH	Initial concentration (mg/L)	Remaining concentration (mg/L)	Removal (%)
GR1	5.68	0.77±0.086	0.323±0.016	58.1
GR2	6.39	1.288±0.163	0.571±0.138	44.3
GR3	6.11	0.627±0.042	0.402±0.023	35.8
GR4	6.37	1.423±0.106	0.866±0.061	39.1

form of anionic borates. At pH 8 hydrated Fe ions still have +3 charges and interact with the boron species of B(OH)₃, the B(OH)₄⁻ with negative charges in aqueous environment. Figure 3 shows the putative representation of borate adsorption on Fe³⁺-PEI polymer.

The effect of Initial Concentration

The effect of initial concentration was carried with 2, 4, 15, 40, 50 mg/L of synthetic solution of boron. The increase of the initial boron concentration enhances the boron adsorption capacity. The highest adsorption ratio was 70.55% which is 56.44 mg B for per gram of dried adsorbent with 40 mg/L solution of boron at pH 8. The adsorption capacity slightly decreases for boron concentration higher than 40 mg/L which can be explained as boron concentration increases available exchangeable sites of polymeric cryogel decreases (Fig. 5).

There are many studies with different polymer supported or modified with chemical agents. Yavuz and colleagues [33] developed a polymeric sorbent with iminopropylene glycol group supported on DHPVC for boron removal and reached an adsorption capacity of 21.62 mg/g for boron. A new boron chelating resin, which the boron adsorption was up to 29.19 mg/g, was synthesized howev-

er the resin was too complex for mass productions [34]. Another polymer which was made of solid tethered imino-bis-propanediol and a functional copolymer had the maximum removal capacity of 43.244 mg/g boron [22].

The polyethylenimine anchored super macro porous polymers indicated their suitability as potential sorbents for boron removal from aqueous solutions and taking advantage from its porous texture, specific surface area and relatively large pore size (10–50 μm), above all not a complex, easy to prepare therefore they are very economic to fabricate [2].

FTIR Results

Obtained FTIR spectra of matrices (with PEI and without PEI) are given in Figure 6. The broad band between the 3300–3400 cm^{-1} indicates –OH stretching vibrations. While band at 1700 cm^{-1} represents vibration of ester group of HEMA, bands at 1515–1535 cm^{-1} is attributed to N–H bending PEI attached to PHEMA cryogel matrix. Besides, the peaks at 1715/cm attributed to stretching vibration of C=O groups in ester of HEMA and GMA.

Removal of Boron in Real Groundwater Samples

The groundwater samples were collected from 4 wells in the area which are used for drinking and irrigation. No pre-adjustments of pH were carried out with the well samples to avoid extra chemical cost for big scale applications. Results were presented in Table 1. Boron species in aqueous solutions usually dependent on the pH of the solution and are present mainly in the form of boric acid and various kinds of borates in, which boric acid dominates at low pH, while borate ion dominates at high pH. In addition, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ mainly exist at low concentration [35].

The most important reason for a successful removal with the Fe^{3+} -PEI polymer, is the dominance of the borate concentration over the other borates at low concentrations and pHs. Borate ions dominated at pH 8 where the highest adsorption was occurred. Please see, Figure 3 shows the putative representation of borate and possible metal ions (i.e., Me^{+1} , $^{+2}$) adsorption on Fe^{3+} -PEI polymer.

Total boron removal rate stayed between 35.8–58.1% at different pH values and the adsorbed amount of boron was found between 9–28.67 (mg/g). WHO guideline values for irrigation water is limited to 0.5 mg /L due to herbicidal effect of boron [9]. Although boron removals were dropped slightly down in real groundwater samples, boron species were reduced to this limit at least in two samples with the polymeric cryogels adsorption. Sample 2 was slightly over whereas, sample 4 only reduced down to 0.8 mg/L with 39.1% adsorption rate. This may be attributed to the presence of other ions in the samples. In the study of Onorato et al. [36] boron removal with being present other ions was found as 47% at pH 10. Glyci-

dol-functionalized macroporous polymer was subjected for boron removal and the maximum adsorption was recorded 29.22 mg/g with the presence of some ions [27]. In the study of Landsman [26] boron adsorption from neutral water was found 2.5 mmol B/g (about 27 mg/g) which was found better than commercial boron selective resin. Amberlite IRA743 previously reported capacity (0.99 mmol B/g dry polymer).

Although boron level suggested to 0.5 mg/L for irrigation by WHO, the boron concentration has to be reduced to 0.3 mg/L in waters that used to irrigate vulnerable plants. Against boron accumulation in soil, actions have to be put into practice especially those affected by low soil leaching in arid regions [37]. Boron toxicity, symptoms mostly occur in spring and are identical to those in drought affected plants. A range of damage threshold values for crops is reported in the literature, from 0.5 ppm to 1.0 ppm [38]. All groundwater samples have elevated boron levels; second and fourth sampling wells were unsuitable for crops because of their high boron compounds over suggested level.

Regeneration of Adsorbent

0.01 M NaOH solution was used for regeneration purposes of boron loaded columns, adsorption-desorption cycles were performed 15-times successfully only with a loss of 5% in adsorption capacity. After 15 cycle boron adsorption-desorption cycle, adsorption capacity decreased. Data is not given here because it is similar to our previous study [2] using the exact polymeric cryogel columns to remove arsenic species from real groundwater samples.

Glycidol-functionalized macroporous polymer was eluted with 1 mol/L HCl and NaOH and regenerated 5 adsorption-desorption cycles, afterwards the adsorption capacity of the polymer was found decreased slightly [27]. The membranes of epoxy-amine cross-linked poly (glycidyl glycidyl ether) (PGGE) were regenerated in acid without a significant loss of boron sorption capacity over four cycles [26]. The polymer was eluted with 1.0 M (cycles 2–4) hydrochloric acid to desorb the boron. Another adsorbent (High internal phase emulsion hierarchical porous polymer) was treated with acid, alkali and the regenerated for 10 cycles for the boron uptake [39].

CONCLUSIONS

Fe^{3+} -attached poly (HEMA-co-GMA)-PEI columns were employed to adsorb boron and boron derivatives from aqueous solution. The maximum adsorption was recorded at pH 8 (54.42 mg/g) with synthetic solution whereas the highest adsorbed concentration was found 28.67 (mg/g) pH 6.39 with real groundwater sample (GR2). Sufficient column regeneration cycles enable the polymer to be suitable in industrial use.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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