



New approach for removal of total hardness (Ca^{2+} , Mg^{2+}) from water using commercial polyacrylic acid hydrogel beads, study and application

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ABSTRACT

Adsorption and water treatment of Ca (II) and Mg (II) hardness were investigated via adsorption of metal ions onto commercial polyacrylic acid hydrogel beads as a novel sorbent for metal ions (Ca^{2+} , Mg^{2+}) removal and water treatment. Batch equilibrium technique was carried out under the influence of solution pH, contact time, sorbent dosage, initial metal concentration and competitive study. The maximum metal ions capacity (Ca^{2+} , Mg^{2+}) values were identified as 171.2 and 193.6, respectively. Sorption equilibrium was established in 24 hr and the data were described by both Langmuir and Freundlich models. The potential application of this sorbent for water treatment and metal ions removal from water samples is successfully accomplished.

Key word: Removal, Polyacrylic acid, Hydrogel bead, New approach

1-INTRODUCTION

Hard water minerals such as calcium, magnesium, iron and manganese result in scaling problems and serious failures in pipelines of boilers and heat-transfer equipment. In addition, these divalent ions can react with soap anions decreasing the cleaning efficiency and hence, high consumption of detergents occurred as a result. However, calcium and magnesium are the most common sources of water hardness [1]. Calcium is the most abundant mineral in the human body. Calcium plays vital roles in the structure and function of the human body [2]. It is substantial for intracellular metabolism, bone growth, blood clotting, nerve conduction, muscle contraction and cardiac function [3][4]. However, there is a significant association between calcium level in drinking water and colorectal, gastric and breast cancer [5][6]. Magnesium is a naturally occurring mineral that is found in food and other medical products. The adult human body contains about 25 g of magnesium, about 60% of this quantity is present in bones and 40% is present in muscles and other tissues. However, taking too much supplemental magnesium can result in symptoms of toxicity. These symptoms include a fall in blood pressure, confusion, abnormal cardiac rhythm, muscle weakness, difficulty breathing and deterioration of kidney function [7]. In order to removal the divalent ions (Ca^{2+} , Mg^{2+}) various methods have been widely applied for water softening includes, electrochemical processes [8], Enzyme catalyzed [9], Nanofiltration [10], electro-dialysis [11], ultrasound [12], ultra-filtration [13], ion-exchange [14][15], membranes [16] and pulsed spark discharge

[17]. The two major methods which are typically used to remove hardness from water are lime soda softening and ion exchange softening. The first method is used mostly for municipal purposes [18]. The primary drawbacks of the lime soda method include the production of a large volume of sludge that requires post-treatment, excessive use of chemicals (such as lime soda ash, and caustic soda) and the addition of acids for pH adjustment, which increases operating expenses [19]. The ion exchange process is primarily employed for residential water softening. Experimental studies have found the sodium level in softened water was 2.5 times higher than municipal water [20]. Adsorption is one of the few promising alternatives for this purpose, especially using low-cost sorbents. A three-dimensional super absorption polymer was used as an absorbent for heavy metal ions from water and other aqueous solutions. Polymer like polyacrylic acid, polyacrylamide and its derivatives which have functional groups (such as carboxylic, hydroxyl and amide) can be used as absorbents for metal ions removal via the interaction between the metal ions and these groups [21].

2-Material and Instrumentations

2.1-Instrumentations:

Atomic absorption spectrophotometer (AAS) type (Phoenix-986 AN, England) was used to determine Mg (II) and Ca (II) ions concentration. An Ametrom E. 632 pH meter (Switzerland), fitted with an Ametrom combined glass electrode was calibrated according to conventional methods and used to adjust the pH of the solution in each experiment. Sartorius BL 210 S (Germany), max. 210 g, D 0.1 mg, was used for chemicals and gel beads weighing. A Vernier caliper with 0.01 mm measuring accuracy was used for measurement of the diameter of the gel beads.

2.2-Chemicals and solutions:

A commercial poly acrylic acid (PAA) hydrogel beads have (3.56 mm diameter and 0.0346 g weight) were used in this work. All other chemicals used throughout this study were of analytical reagent grade and were purchased from Aldrich Chemical Company. A 1000 mg / L aqueous solution of Mg (II) and Ca (II) ions were prepared from magnesium sulphate heptahydrate and calcium chloride salts. More dilute solutions of metal ions were prepared from stock solutions by simple dilution with distilled water.

3-Adsorption studies

3.1 Effect of contact time on metal ions removal:

The previously mentioned batch experiment procedure was carried out at different contact times of 2, 4, 8, 12, 24 and 48 hr. The adsorption experiments were conducted at a pH of 6.3 at room temperature (25 ± 2 °C) and solutions concentration of 400 mg.L^{-1} . The residual metal ions concentration after adsorption process was determined by AAS and the metal ions adsorption capacities at each time value were evaluated using the following equation:[22]

$$Q = (C_0 - C_e) V / m \dots\dots 1$$

Where Q is the amount of metal ions adsorbed at time t or at equilibrium (mg / g) that represented the amount of metal ions mg adsorbed per gram of dry gel bead. C_0 , C_e are the initial and final concentration (concentration at t time or at equilibrium) of metal ions (mg.L^{-1}), V is the volume of metal ions solution used (L), and m is the weight of the hydrogel bead used (g).

3.2-Effect of pH on metal ions removal:

All batch experiments were carried out at room temperature and each experiment was performed in 25 ml volumetric flask using 25 ml of 400 mg.L⁻¹ metal ions solution and one hydrogel bead has (0.0346 g) weight. The pH of solution was adjusted at a range of (1- 7) and left for 24 hr contact time. Residual metal ions concentration was determined by AAS and the adsorption capacity was evaluated from equation (1).

3.3-Effect of adsorbent dosage on metal ions removal:

Similar batch experiment were carried out by mixing 25 ml of 1000 mg.L⁻¹ metal ions solution with different number of hydrogel bead 1,2,3,4,5 and 6 have (0.0346, 0.0692, 0.1038, 0.1384, 0.173 and 0.2076 g) weight. The solutions were adjusted at pH of 6.3 and lifted for 24 hr at room temperature. The residual metal ions concentration was determined using AAS and the percentages of metal ions removal and adsorption capacity were then evaluated.

3.4-Effect of initial metal ions concentration on adsorption capacity:

Adsorption equilibrium and isotherm studies were evaluated by varying the initial metal ions concentration. A 25 ml solution of 50, 100, 200, 300 and 400 mg.L⁻¹ metal ions was used at pH of 6.3. The solutions were left at room temperature for 24 hr and the residual metal ions concentration was determined using AAS.

3.5-Competitive adsorption study:

Competitive adsorption of Mg (II) and Ca (II) ions by the PAA hydrogel bead from aqueous solution containing the two ions together was investigated in these two groups of experiment as listed in Table 1. The adsorption experiments were carried out at pH of 6.3 at room temperature and 24 hr contact time. The adsorption capacities of hydrogel bead were evaluated using equation 1 and the following equation for selectivity percentage (SP):[23]

$$\% \text{ SP} = \frac{\text{amount of metal ion adsorbed}}{\text{total amount of adsorbed metal ions}} \times 100 \dots\dots\dots 2$$

Table. 1. The mixture of metal ions in competitive study.

Experiment 1		Experiment 2	
Metal ion	Concentration mg.L ⁻¹	Metal ion	Concentration mg.L ⁻¹
Mg / Ca		Ca / Mg	
	100/100		100/100
	200/100		200/100
	300/100		300/100
	400/100		400/100

4-Results and discussion

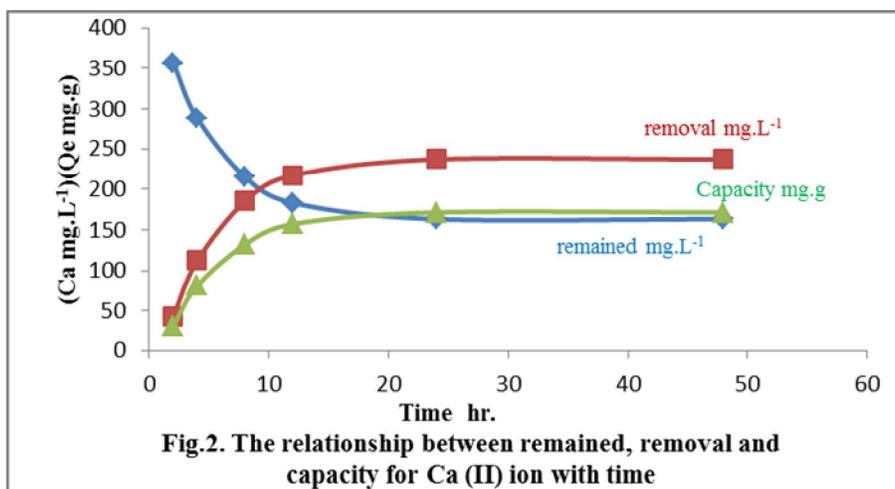
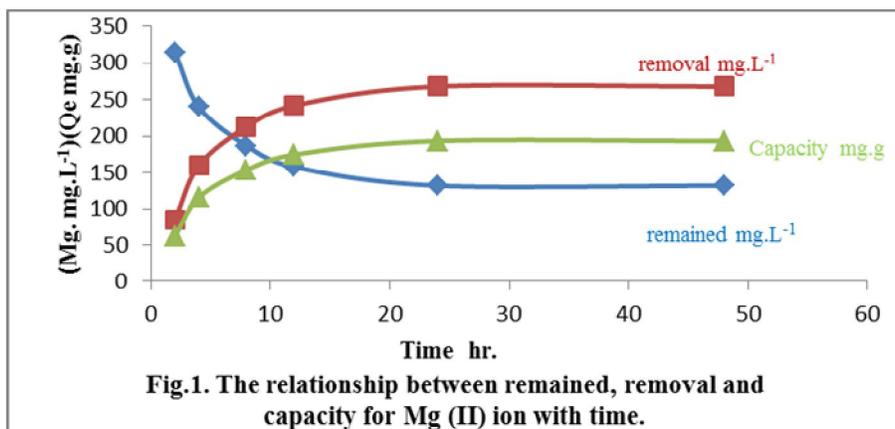
All the results obtained are tabulated in Tables 2- 10.

4.1-Effect of contact time:

Adsorption capacities and removal metal ions (Table 2) of Mg (II) and Ca (II) as function of contact time are shown in Fig. 1 and 2. The adsorption of both two ions in PAA hydrogel beads was identified to proceed via two successive steps. In the initial step, the removal efficiencies of both Mg (II) and Ca (II) increased rapidly due to the abundant availability of active binding sites on sorbent surface. With the gradual occupancy of these sites, the adsorption process becomes less efficient due to a complete saturation of the surface with metal ions in a later step. One of the vital advantages of this sorbent is the large adsorption capacity (i.e. 1 Kg of Mg (II) ion in water need about 0.179 Kg of gel bead for its removal).

Table. 2. Summary of the result obtained from the contact time study.

Time hr.	Mg (II) ion			Ca (II)		
	Remained mg.L ⁻¹	Removal mg.L ⁻¹	Capacity mg.g	Remained mg.L ⁻¹	Removal mg.L ⁻¹	Capacity mg.g
2	315	85	61.4	357	43	31.1
4	240	160	115.6	288	112	80.9
8	187	213	153.9	215	185	132.2
12	158	242	174.9	183	217	156.8
24	132	268	193.6	163	237	171.2
48	132	268	193.6	163	237	171.2

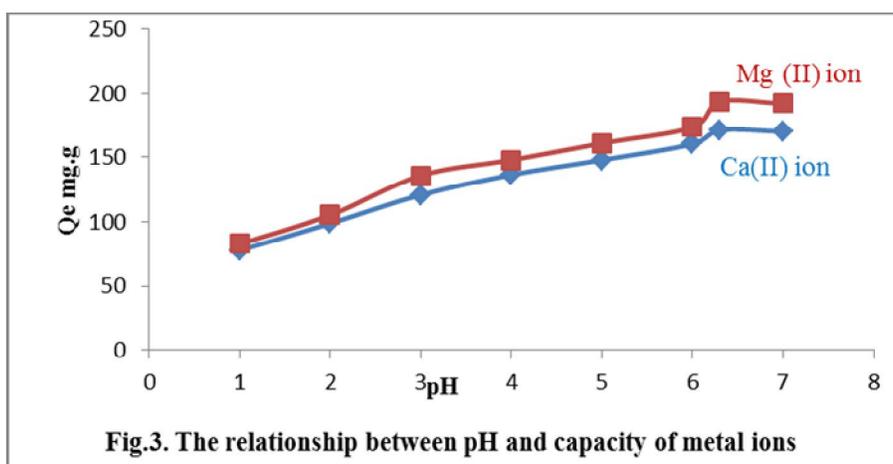


4.2-Effect of pH:

The pH of metal ion solutions is considered as the most substantial parameter affecting the adsorption behavior of metal ions from aqueous solution. The variation of hydrogen ion concentration affects the number of metal ions binding sites on the adsorbent surface. The determined metal ions capacities values at different pH, are listed in Table 3. Fig. 3 shown that the values of the metal ions adsorption capacity are increased with the increase in the solution pH till it reached this maximum value at pH 6.3. That may be due to the high degree of deprotonation of the functional group on the surface of hydrogel bead occurs at high value of pH. [24]

Table. 3. The results obtained from the effect of pH study.

pH	Mg (II)		Ca (II)	
	Removal mg.L ⁻¹	Capacity mg.g	Removal mg.L ⁻¹	Capacity mg.g
1	115	83.1	108	78
2	146	105.5	137	98.9
3	188	135.8	168	121.4
4	205	148.1	189	136.6
5	223	161.1	205	148.1
6	240	173.4	222	160.4
DW	268	193.6	237	171.2
6.3				
7	266	192	235	170



4.3-Effect of adsorbent dosage:

The number of available active binding sites on the adsorbent surface, represented by adsorbent mass effect on Mg (II) and Ca (II) ions adsorption capacity values and percentage of metal ions removal, was studied as listed in Table 4. The percentage of metal ions removal was found to increase with increasing adsorbent mass due to the existence of larger surface area as well as greater number of active binding sites as shown in Fig. 4.

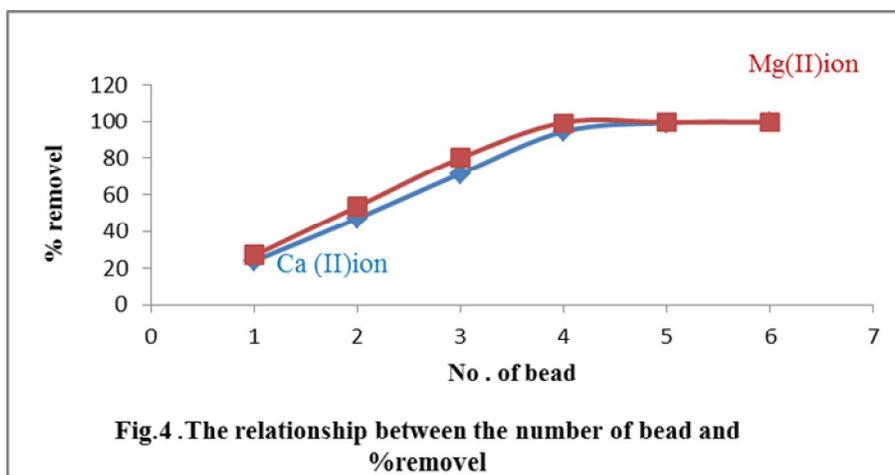


Table. 4. Results of the adsorbent dosage effect study.

No. of bead Weight (g)	Mg(II) removal%	Ca(II) removal%
1 (0.0346)	27%	24%
2 (0.0692)	53.5%	47%
3 (0.1038)	80%	71.4%
4 (0.1384)	99.5%	94.5%
5 (0.1730)	99.6%	99.3%
6 (0.2076)	99.8%	99.6%

4.4-Effect of initial metal ion concentration (adsorption equilibrium and isotherm study):

Adsorption isotherm describe the equilibrium process of a metal ions at the surface of the solid sorbent and represent the relationship between the amount of metal ion adsorbed per unit mass of solid sorbent and its concentration in the equilibrium solution at constant temperature. The elucidation of isotherm data by fitting them to different models is a substantial step in the adsorption study. Langmuir and Freundlich models are the most widely used models in case of the adsorption of metal ions with solid sorbent. The Langmuir isotherm is given by equation (4) and Freundlich isotherm is given by equation (5) as following:[25]

$$\text{Langmuir equation: } C_e / Q_e = 1 / Q_{\max} K_L + C_e / Q_{\max} \dots\dots\dots 4$$

$$\text{Freundlich equation: } \text{Log } Q_e = K_F + 1 / n \text{ log } C_e \dots\dots\dots 5$$

Where Q_e is the amount of metal adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of metal solution mg.L^{-1} , Q_{\max} is the maximum capacity of adsorption (mg/g) and K_L is the Langmuir adsorption constant (L/g) and is related to the free energy of adsorption, K_f (ml/g) and n are the Freundlich adsorption isotherm constants, being indicative of the adsorption extent and the degree of nonlinearity between solution concentration and adsorption, respectively. The identified isotherm constant and capacity parameters, for metal ions are listed in Table 5, Table 6 and Table 7 respectively, which are useful in providing information about the effectiveness of the metal-adsorption system. In view of the value of linear regression coefficients (R^2), it was found

that the adsorption process for the Mg (II) and Ca (II) ions is well described and more fitted with Langmuir rather than Freundlich isotherm as shown in Fig. 5, Fig. 6, Fig. 7, Fig. 8 and Fig. 9.

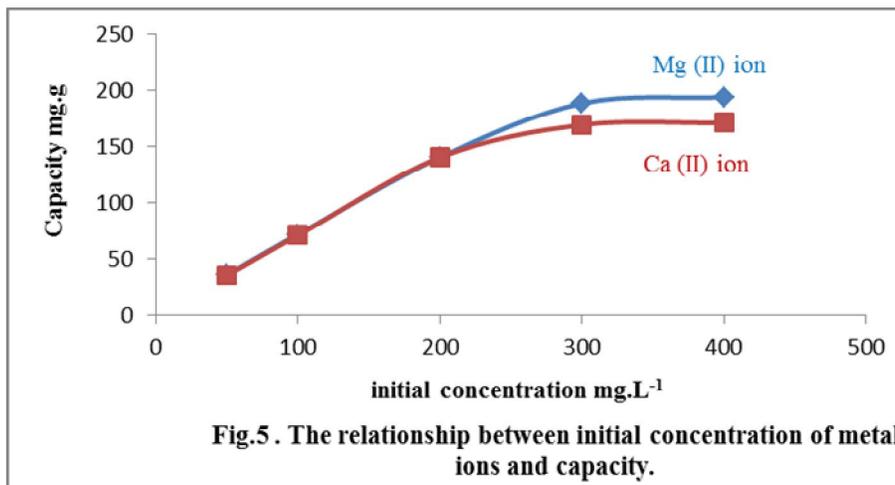
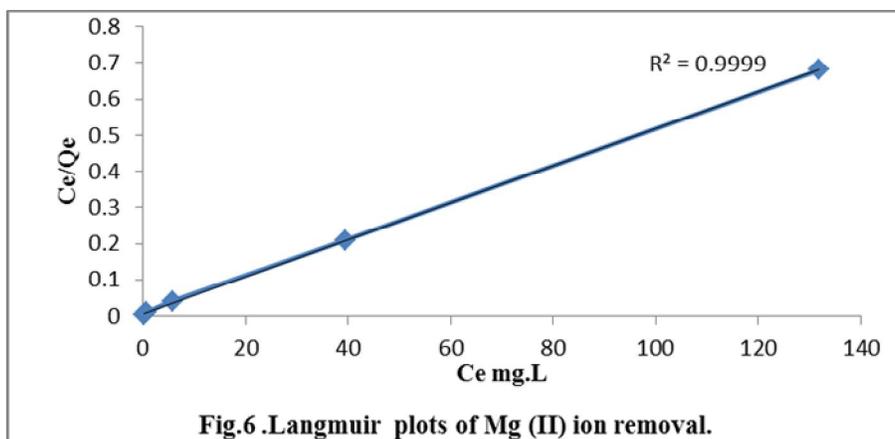


Table. 5. Summary of the results obtained from initial ions concentration effect study.

Initial ions concentration mg.L ⁻¹	Mg (II) ion		Ca (II) ion	
	Removal mg.L ⁻¹	Capacity mg.g	Removal mg.L ⁻¹	Capacity mg.g
50	49.9	36.1	49.2	35.5
100	99.3	71.7	98.3	70.8
200	194.2	140.3	194	140.2
300	260.5	188.2	235	169.1
400	268.2	193.8	236.5	170.9



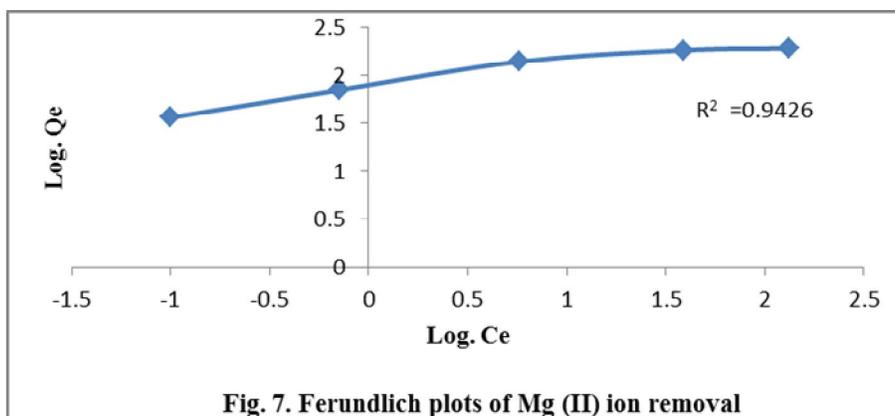
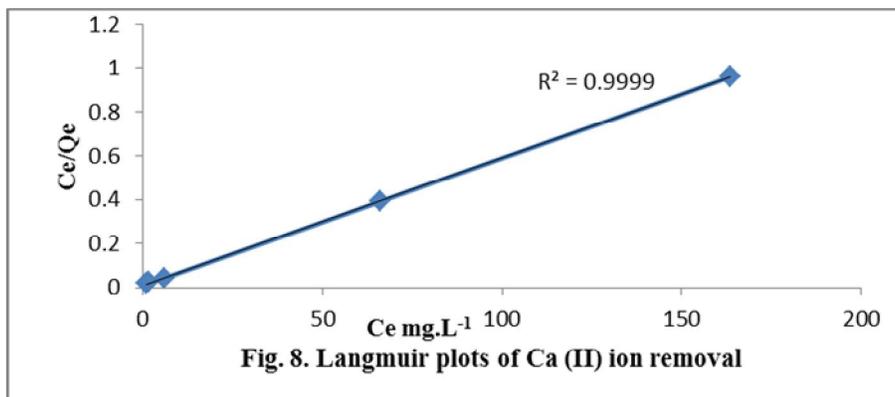


Table.6. Estimated adsorption isotherm parameters of Mg (II) removal.

Langmuir model			Freundlich model		
Q_{max} (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2
196.1	0.7611	0.9999	6.45	4.16	0.9426



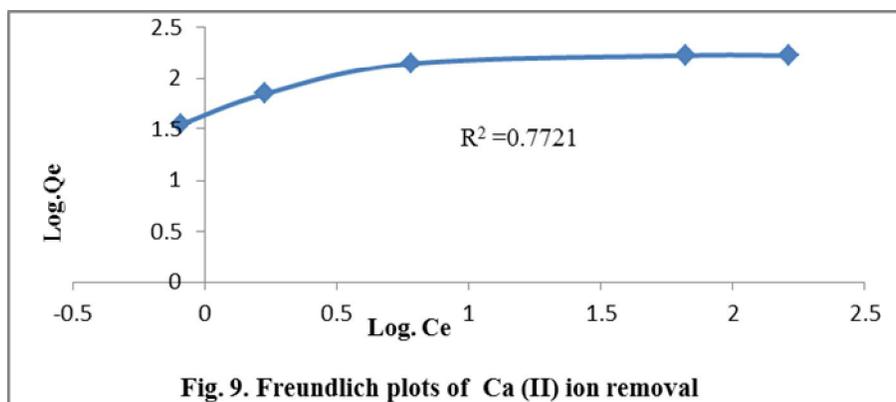
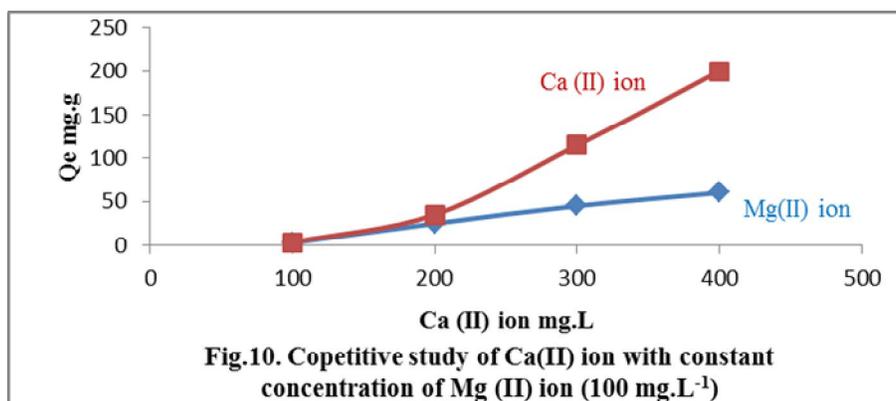


Table .7. Estimated adsorption isotherm parameters of Ca (II) removal.

Langmuir model			Freundlich model		
Q_{max} (mg/g)	K_L (L/mg)	R^2	K_f (L/g)	n	R^2
172.4	0.4874	0.9999	5.71	3.81	0.7721

4.5-Competitive adsorption:

The results of this study, compiled in Table 8 and Table 9, showed that the presence of each metal ion in a high concentration and constant low concentration for the other ion exhibited limit effect on adsorption capacity of the metal ions especially at high concentration. The results also indicated that the value of adsorption capacity for Mg (II) ion was still higher than that for Ca (II) ion as shown in Fig.10, Fig.11, Fig. 12 and Fig. 13. The selectivity percentages are given in the top of bars in the Fig. 12 and Fig .13.



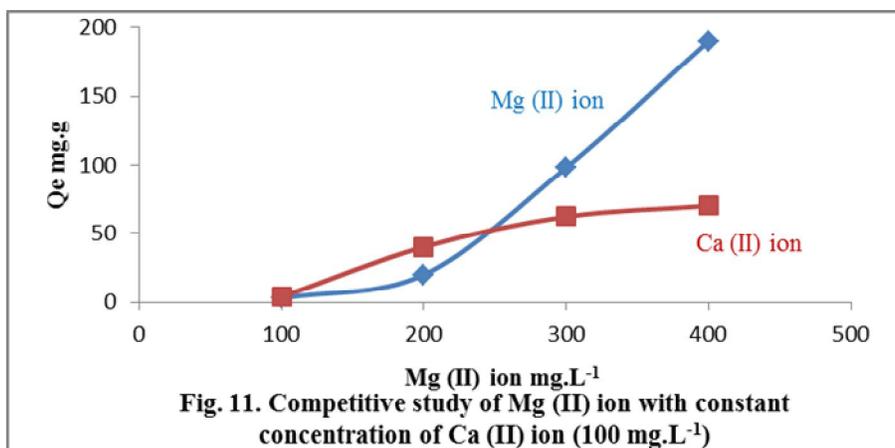
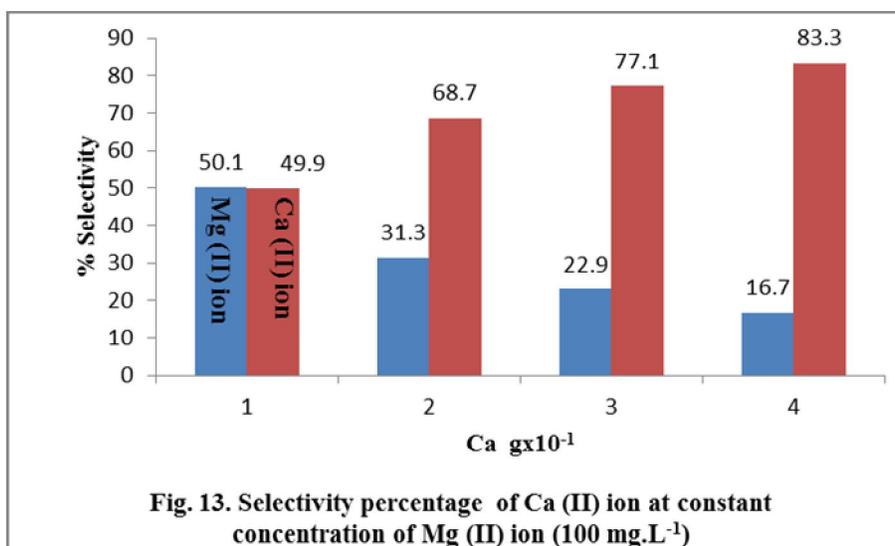
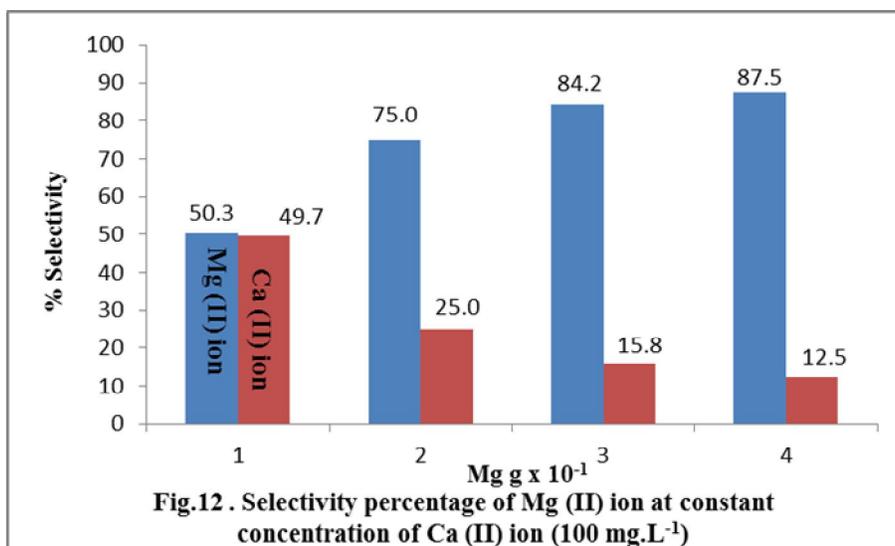


Table. 8. The values of adsorption capacity.

Experiment 1			Experiment 2		
Metal ion Concentration mg.L ⁻¹ Mg / Ca	Capacity mg.g		Metal ion Concentration mg.L ⁻¹ Ca / Mg	Capacity mg.g	
	Mg (II)	Ca (II)		Mg (II)	Ca (II)
100/100	70.1	69.4	100/100	70.2	69.7
200/100	130.1	43.4	200/100	54.2	119.2
300/100	145.9	27.5	300/100	39.7	133.6
400/100	151.7	21.7	400/100	28.9	144.5

Table. 9. The values of selectivity percentage.

Experiment 1			Experiment 2		
Metal ion Concentration mg.L ⁻¹ Mg / Ca	Selectivity %		Metal ion Concentration mg.L ⁻¹ Ca / Mg	Selectivity %	
	Mg (II)	Ca (II)		Mg (II)	Ca (II)
100/100	50.26	49.74	100/100	50.13	49.87
200/100	75.00	25.00	200/100	31.25	68.75
300/100	84.17	15.83	300/100	22.92	77.08
400/100	87.5	12.5	400/100	16.67	83.33



4.6-Water treatment of Mg (II) and Ca (II) ions removal from real hard water sample:

A hard tap water samples obtained from three sources of water in Baghdad and Wasit were studied for water treatment and removal of magnesium and calcium by the use of PAA hydrogel beads. The hard water samples were first analyzed for the original Mg (II) and Ca (II) ions contain by AAS, then the removal of metal ions was carried out by left a 100 ml of water sample with one hydrogel bead has 0.0346 g weight at room temperature for 4 hr. The residual metal ions concentration was determined by AAS and the removal percentage of metal ions (RP) was determined on the basis of triplicate analysis (Table. 10) according the following equation:

$$\%RP = \frac{\text{initial concentration} - \text{residual concentration}}{\text{initial concentration}} \times 100 \dots\dots\dots 6$$

Table.10 . Summary of the results for water treatment study.

Sample area (tap water)	Metal ions concentration mg.L ⁻¹					
	Before treatment		After treatment		Removal percentage	
	Mg (II) ion	Ca (II) ion	Mg (II) ion	Ca (II) ion	Mg (II) ion	Ca (II) ion
Baghdad (New Baghdad)	50	55	2.4	3.3	95.2	94.0
Baghdad (Al-kaheera)	17	23	0.6	1.2	96.5	94.8
Wasit (Kute)	28	33	1.2	2.1	95.7	93.6

The results in Table are elucidate great improving in the water- softening from magnesium and calcium by using PAA hydrogel beads as adsorbent.

5-Conclusion:

The adsorption of metal ions [Mg (II) and Ca (II) ions] on PAA hydrogel bead was successfully achieved and confirmed for development a highly effective adsorbent. The adsorption efficiency of the adsorbent for removal of Mg (II) and Ca (II) ions from aqueous solution was studied by using the batch process under influence of different parameters. The maximum adsorption capacity values of metal ions were identified at pH 6.3. The data of equilibrium was well described by both Langmuir and Freundlich models. Application of the method for natural tap water- softening and treatment was successfully accomplished.

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