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Removal and Preconcentration of Calcium from Industrial Water by Synthesis of Ionic Imprinted Polymer

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Abstract

Removal and preconcentration of Calcium from industrial water By employing several monomers, including Styrene and 1-vinyl imidazole, bulk polymerization was used to create unique Calcium (II) ion-imprinted polymers (IIPs). To achieve the highest adsorption capacity, the molar ratios of the template, monomer, cross-linking agent, solvents, and different monomers for polymerization were studied. scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Fourier-transform infrared spectroscopy (FTIR) were used to characterize the produced calcium-IIPs. The maximum capacity for calcium-IIP adsorption was 222.1 mol/g for calcium-IIP2 and 272.6 mol/g for calcium-IIP1 (both of which used styrene as a monomer). Calcium-IIP adsorption complied with Langmuir isotherm models. Before and after treatment, samples of industrial water are obtained from refineries to eliminate chemical components from the water. These solutions were filtered via a 0.5 m filter before being added to the Calcium-IIP-SPE packed column system. to eliminate calcium ions and measure them.

Keywords: Industrial water, calcium ion imprinted polymer, adsorption, pre-concentration, solid phase extraction.

إزالة الكالسيوم وتركيزه المسبق من المياه الصناعية عن طريق تخليق البوليمر المطبوع الأيوني

الخلاصة

لاعادة تركيز وازالة ايونات الكالسيوم من المياه الصناعية تم تحضير بوليمرات الطبعة الايونية جديدة للكالسيوم (II) بواسطة البلمرة الكتلية باستخدام أنواع مختلفة من المونومرات مثل الستايرين و 1- فينيل إيميدازول، على التوالي. تمت دراسة النسب المولية للقالب والمونومر والرابط المتقاطع للبلمرة والمذيبات والعديد من المونومرات للحصول على أكبر قدرة امتصاص. تم دراسة خصائص البوليكات المحضرة Calcium-IIPs المحضر باستخدام مطيافية الأشعة تحت الحمراء (FTIR)، والمسح المجهري الإلكتروني (SEM) والتحليل الطيفي للأشعة السينية المشتتة للطاقة (EDX). كانت أعلى سعة لامتصاص الكالسيوم هي 272.6 ل Calcium-IIP1 (باستخدام الستايرين كمونومر) و µmol/g 222. ميكرو مول/غم Calcium-IIP2 (باستخدام 1-فينيل إيميدازول كمونومر). وبعد ذلك تم دراسة الموديل الرياضي الامتزاز الخاص بـ Calcium -IIPs بواسطة Langmuir isotherm models. أخذت عينات من المياه الصناعية من المصافي قبل وبعد المعالجة لإزالة المكونات الكيميائية من المياه. تمت تصفيته بفلتر 0.5 ميكرومتر، ثم تم إدخال هذه المحاليل في نظام العمود المعبأ Calcium-IIP-SPE، لازالة ايونات الكالسيوم وتقديرها.

1. Introduction

In recent years, industrial wastewater and hypersaline water (HW) have become more often used in place of freshwater in industrial operations in places where freshwater is in short supply. HW has long been employed as a coolant in steel manufacturing, petrochemical production, and nuclear and thermal power plants. However, secondary ions like calcium ions (Ca^{2+}) are always present in HW and are extremely hazardous to industrial processes because limescale is easily formed by Ca^{2+} ions in cooling systems, reverse osmosis plants, mining, and other industries. As a result, industrial production costs rise and efficiency decreases. Due to the size issue, replacing and repairing pipes and other infrastructure costs millions of dollars each year. Additionally, when limescale particles enter the stomach, they react with the hydrochloric acid to release Ca^{2+} ions and carbon dioxide (CO_2). The former of these two substances may cause illnesses like kidney and ureteral stones, while the latter could result in stomach perforation in people who have stomach ulcers. To provide secure industrial production and to safeguard human health, a lesser degree of Ca^{2+} ion concentration reduction in HW is necessary [1]. There are four types of methods for removing Ca^{2+} ions from HW; they are, chemical, physical, biological, and physicochemical methods [2]. These common technologies do, however, have several drawbacks, including the fact that they are only appropriate for basic systems, secondary pollutants, limited service lives, low processing speeds, poor selectivity, high costs, and high energy consumption. Therefore, there is a dire need for the creation of a pollution-free method that is inexpensive, practical, and has both high selectivity and adsorption capacity [3]. Innovative chemical separation methods have been created as a result of recent advancements in analytical chemistry and are now crucial. The development of novel extractants and adsorbents has been fueled by the demand for a more selective system for metal ion separation [4]. Researchers are now interested in the selective preconcentration of the sorbents used in solid-phase extraction (SPE). This fairness is crucial when examining complicated matrices like effluent or river water samples [5].

Compared to conventional liquid-liquid extraction, SPE is quicker, cheaper, more efficient, and more ecologically friendly. The fundamental problem with SPE columns filled with conventional stationary phases is the low selectivity of the retention mechanism. To attain the required degree of selectivity, columns containing materials based on molecularly imprinted polymers (MIPs) as selective sorbents can be utilized [6-8].

A specific technology called molecular imprinting is made possible by accurate identification. A molecularly imprinted polymer is made by first mixing the template molecules with functional monomers. Crosslinking agents and initiators are then added in order to initiate polymerization. A chemical or physical procedure then gets rid of the template molecules. When a molecularly imprinted polymer contains space gaps that are correctly matched with the target molecules, it is undeniably fully prepared. [9-12].

Ion-imprinted polymer (IIP), a synthetic sorbent for metal ions that is linked to MIPs but can also detect inorganic ions, was created [13]. Various methods, such as bulk polymerization [14], surface imprinted technique [15] precipitation polymerization [16], sol-gel polymerization [17, 18], and suspension polymerization [19, 20] have been used for the preparation of ion imprinted polymers.

In this study, two different types of calcium (II)-IIPs were created by bulk polymerization using calcium chloride ($CaCl_2$) as a templet, styrene, and 1-vinyl imidazole as monomers. Ethylene glycol dimethacrylate (EGDMA) was used as a crosslinker and benzyl peroxide served as an initiator to remove the Ca(II) ions from the aqueous. On the effectiveness of adsorption, the effects of monomer and EGDMA doses were examined. Investigated were the adsorption characteristics of several functional monomers, cross-linking agents, and solvents. The prepared IIPs were characterized using SEM, FTIR, and EDX. Additionally, the impacts of adsorption parameters on adsorption capacity were investigated. These factors included adsorption period, flow rate of solution passing through a solid phase extraction syringe, and starting Ca(II) concentration.

2. Material and methods

2.1. Reagents and Chemicals

Styrene, 1-vinyl imidazole, ethylene glycol dimethacrylate (EGDMA), and benzyl peroxide were supplied by Sigma-Aldrich (St. Louis, USA, Missouri, www.sigma-aldrich.com); methanol, chloroform, acetonitrile, and acetic acid were supplied by Merck (Germany, Darmstadt, www.merck.com). Calcium chloride, or CaCl2 from British Drug Houses (BDH). The Arab Gulf is supplied with nitrogen gas (99.99%) from a Baghdad plant.

2.2. Instrument

The control procedure involved the use of an atomic absorption spectrophotometer PGinstrument (England), a UV 1800pc spectrophotometer (Shimadzu, Japan), a scanning electron microscope (SEM) and an EDX MIRA3 TESCAN (Czechoslovakia), an FTIR FTIR 8000 (Shimadzu, Japan), and ultrasonic (W. Germany) to stir the copolymer solution.

2.3. Preparation of ionic imprinted polymer

A little quantity of methanol was used to dissolve 1 mmol (0.111 g) of calcium chloride ($CaCl_2$) before it was combined with 20 mmol (2.08 g) of styrene as the monomer and 40 mmol (7.92 g) of EGDMA as the crosslinker to create the first calcium ionic imprinted polymer (Ca-IIP1). All of these components were diluted in 5 mL of CH3OH, and 0.3 mmol (0.07 g) of benzoyl peroxide was then added as an initiator after being dissolved in 5 mL of chloroform. The mixture was agitated for 5 minutes in order to produce a homogenous solution. The second Calcium ionic imprinted polymer (Ca-IIP2) was made by combining 1 mmol (0.111 g) of Calcium Chloride ($CaCl_2$) as a template, 20 mmol (1.88 g) of 1-vinyl imidazole as the monomer, and 40 mmol (7.92 g) of EGDMA as the crosslinker to the solution, all of these components were mixed in 5 mL of methanol (CH_3OH), and 0.36 mmol (0.08 g) of benzoyl peroxide was added to the mixture as the initiator after being dissolved in 5 mL of chloroform ($CHCl_3$). The mixture was then agitated to create a homogenous solution. To eliminate oxygen from the combination of the two polymers (Ca-IIP1 and Ca-IIP2), nitrogen gas was passed over it for 30 minutes. The solution was then heated in a water bath at 60°C for 4 hours. The ionic imprinted polymer becomes solidified after the process is finished. Following the polymerization procedure, they were allowed to cure for 24 hours before being crushed and ground into particles with a sieve that had a diameter of 125–150 µm. To remove the template from IIPs, these particles were extracted in a soxhlet using 100 mL of CH_3OH: CH_3COOH (10:1 v/v). The polymer was collected and allowed to dry for 24 hours at room temperature before being utilized as a component in a solid-phase extraction syringe. The same components and conditions are used to create non-ionic imprinted polymers as for Ca-IIP1 and Ca-IIP2, but $CaCl_2$ is not used (template). In order to create non-imprinted polymers (NIPs), the same distribution was used, but there was no template. The same distribution was used to create non-imprinted polymers (NIPs), which did not contain a template.

2.4. The Sampling Device

We utilized 3 ml solid phase extraction syringes, and we filled each one with various weights (0.1 and 0.2gm) of MIP.

2.5. Sampling Procedure

Create a stock solution of calcium chloride ($CaCl_2$) at a concentration of 1, 10, 20, 30, 40, 50, 60, 70, 80 ppm, and dilute solution of 1 ppm to create 0.1, 0.5, 1, 2, 3, 4, 5, 10, 15, 20, and 25 ng/ml for a pre-concentration method to determine the small amount that is difficult to detect in a flame atomic absorption spectrophotometer.

Additionally, multiple samples of industrial water before and after treatment were delivered to refineries to wash crude oil to remove salts before the refining process.

2.6. Extraction and digestion procedure

By employing a solid phase extraction (SPE) syringe and calcium-IIP1 and calcium-IIP2, calcium ions were extracted from synthetic solutions, diluted synthetic solutions, and industrial water and delivered to refineries. This syringe was made by fitting an IIP, 0.2mg, inside a container that was 5ml in size. A peristaltic pump is used in a vacuum process to move the calcium-containing solution through a SPE syringe at a variable pace. IIP was extracted from the column into a small beaker and allowed to dry for 60 minutes. After that, it was treated with concentrated sulfuric and nitric acids for 1 and 8 minutes, respectively, before being mixed with deionized water and directly measured by a flame atomic absorption spectrophotometer.

3. Result and Dissection

3.1. Characterizations

3.1.1. FT-IR

The relationship between the Ca ion and the monomer was confirmed using spectral analysis. The FT-IR spectra were detected using the Cesium Iodide (CsI) pellet method between 250 and 4000 cm-1. Figure 1 depicts Ca-IIP1 before and after elution. As can be observed, the backbones of both spectra (A, B) are comparable, indicating that the elution procedure had little to no impact on the main structure of the polymer network.

Strong bands at 1627.81 and 522.67 cm-1 in the spectra of Ca-IIP1 before elution, which correspond to the Ca-O and Ca-Cl groups, show that calcium chloride was involved in the synthesis of Ca-IIP1. Due to the breakdown of the initial connection between styrene and Calcium, these two peaks vanish after eluting Ca ions, demonstrating that Calcium ions had been properly eliminated.

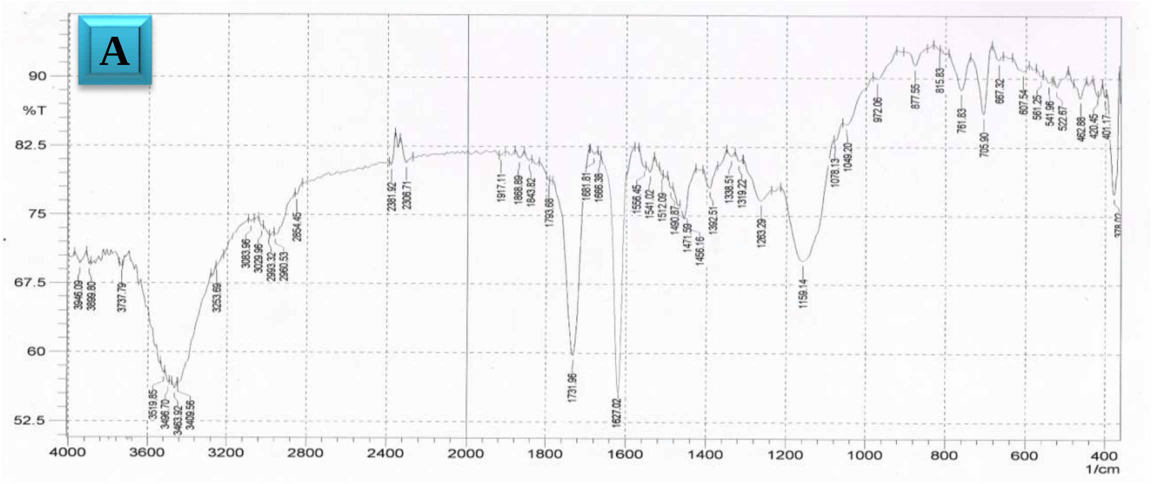
Figure (2) depicts the FT-IR spectra of Calcium-IIP2, with a band at 1626.50 and 495.67 cm-1 that corresponds to the Ca-O and Ca-Cl groups. Following the elution of calcium ions, these two peaks vanish as a result of the breakdown of the first contact between 1-vinyl imidazole and the Ca ion. The data in Tables (1) and (2) are used to determine the major peaks.

3.1.2. SEM

Determining the size and configuration of regions where the Calcium ion has been eliminated requires morphological examination.

By using SEM pictures, the shape of the Ca-IIPs was assessed. The surface morphologies of the particles for Ca-IIP1 are depicted in Figures (3A and 3B) before and after elution. Due to the elimination of calcium ions, it can be noticed that the surface of eluted Ca-IIP1 has holes and is rougher than the surface of the non-eluted one.

Figure (4 A, B) depicts the surface morphologies of Ca-IIP2 both before and after elution. Due to the many holes on the surface of two different types of manufactured IIPs and the well-defined binding sites on the imprinted polymer, these materials are ideal sorbents. Additionally, the photos demonstrate that the sizes and shapes of pores with diameters between (350-400 nm) for Calcium-IIP1 and (400-450 nm) for Calcium-IIP2 are non-uniform (irregular).



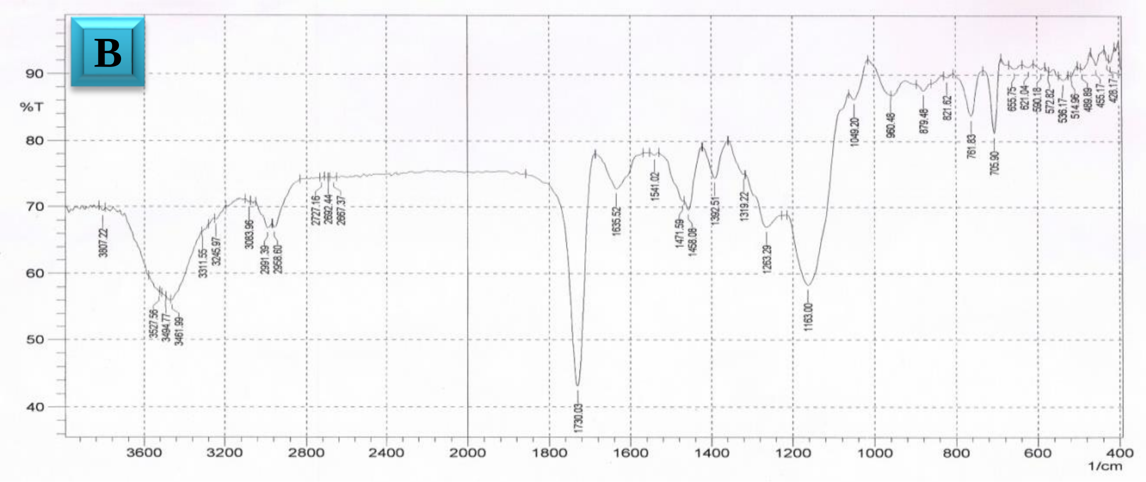


Fig. (1): FTIR spectrum of Ca-IIP1.
A. before the Ca ion was removed B. after the Ca ion has been removed

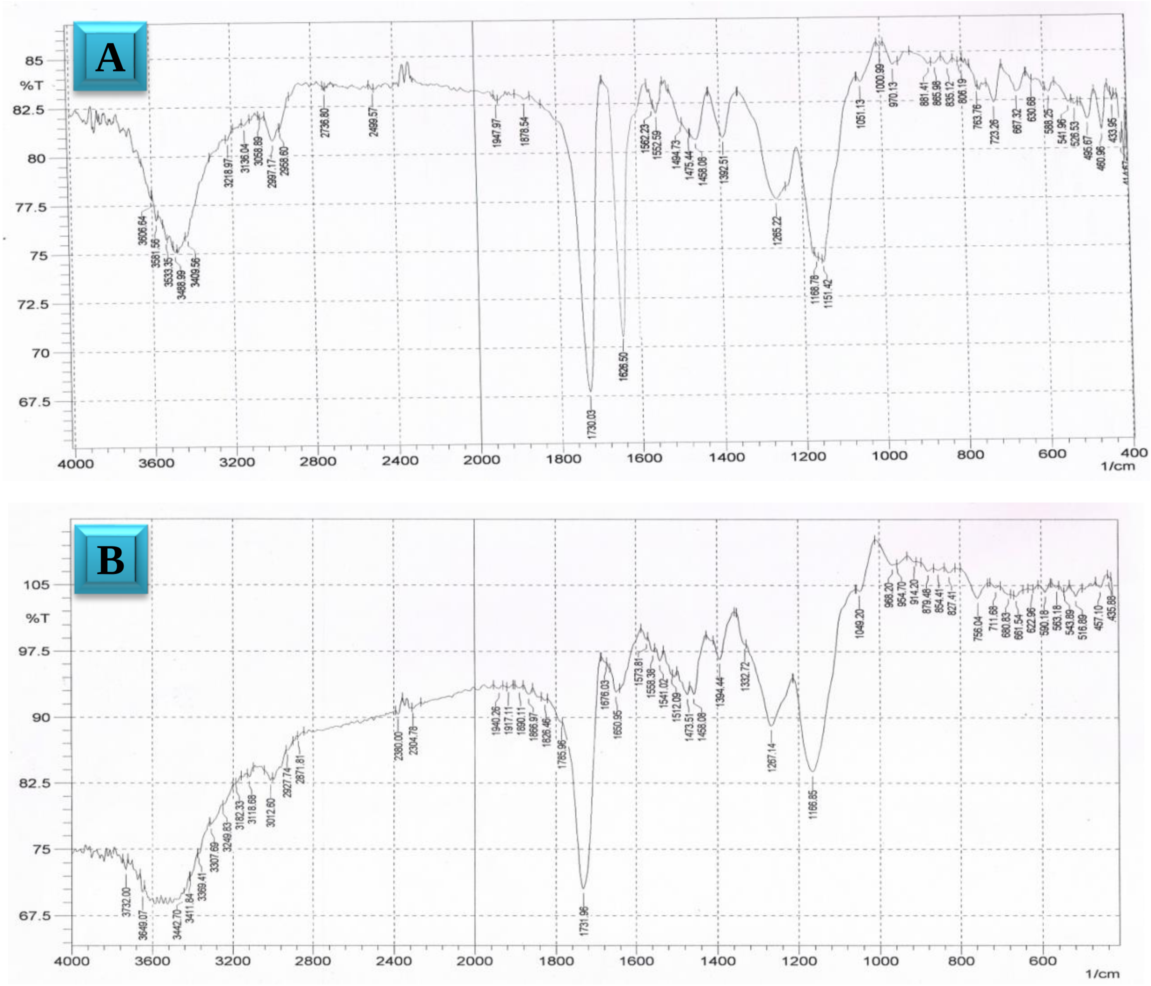


Fig. (2): FTIR spectrum of Ca-IIP2
A. before the Ca ion was removed B. after the Ca ion has been removed

Table (1): FTIR spectrum Calcium-IIP1's most often recognized peaks

NO	Functional Group	$CaCl_2$(cm^{-1})	Ca-IIP1 before templet removal (cm^{-1})	Ca-IIP1 after templet removal (cm^{-1})
1	C-H aliphatic	-----	2960.53 2993.32	2991.39 2958.60
2	C=O ester	-----	1731.96	1730.03
3	C-H aromatic	-----	3029.96	3083.96
4	C=C aliphatic	-----	1556.45	1541.02
5	C-O	-----	1263.29	1263.29
6	Ca-O	1627.81	1627.02	------
7	Ca-Cl	522.62	522.67	------

Table (2): FTIR spectrum Calcium-IIP2's most often recognized peaks

NO	Functional Group	$CaCl_2$(cm^{-1})	Ca-IIP2 before templet removal (cm^{-1})	Ca-IIP2 after templet removal (cm^{-1})
1	C-H aliphatic	-----	2958.6 2997.17	2927.74 2871.81
2	C=O ester	-----	1730.03	1731.96
3	C-H aromatic	-----	3058.89	3012.60
4	C=C aliphatic	-----	1552.59	1558.38
5	C-O	-----	1265.22	1267.14
6	C-N	-----	1458.08	1458.08
7	Ca-O	1627.81	1626.50	------
8	Ca-Cl	522.62	526.53	------

3.1.3. EDX

The composition of Ca-IIPs was ascertained using the EDX test, which also served as evidence that the calcium ion was effectively eluted. The EDX spectra of Ca-IIPs are depicted in Figures (5 A, B) and (6 A, B) before and after elution. Ca ions are definitely present in the structure, according to the findings in Figures (5 A) and (6 A). As can be seen in (5 B) and (6 B), the calcium ion is not present in the structure of calcium-IIPs after elution, proving that the porogen solvent CH3OH/CH3COOH (10:1 v/v) was successful in eluting the calcium ion.

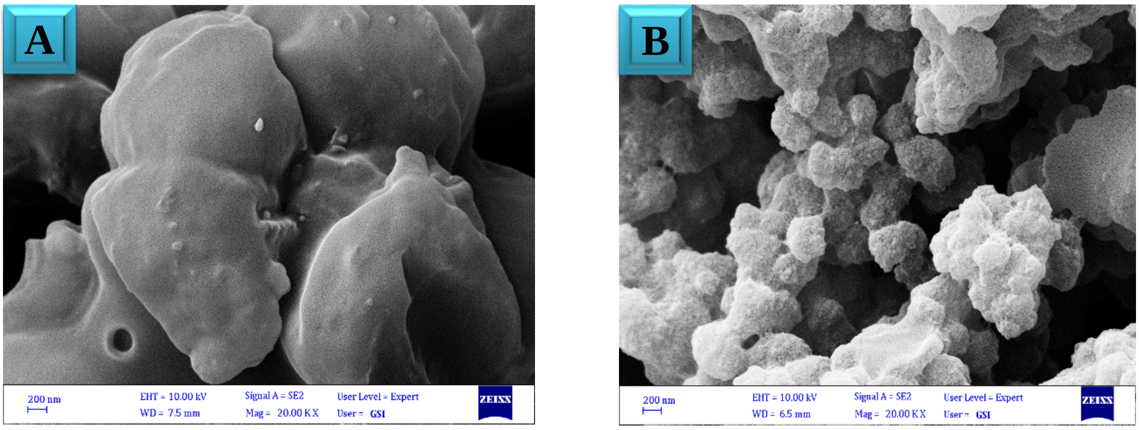


Fig. (3): SEM of Ca-IIP1
A. before the Ca ion was removed B. after the Ca ion has been removed

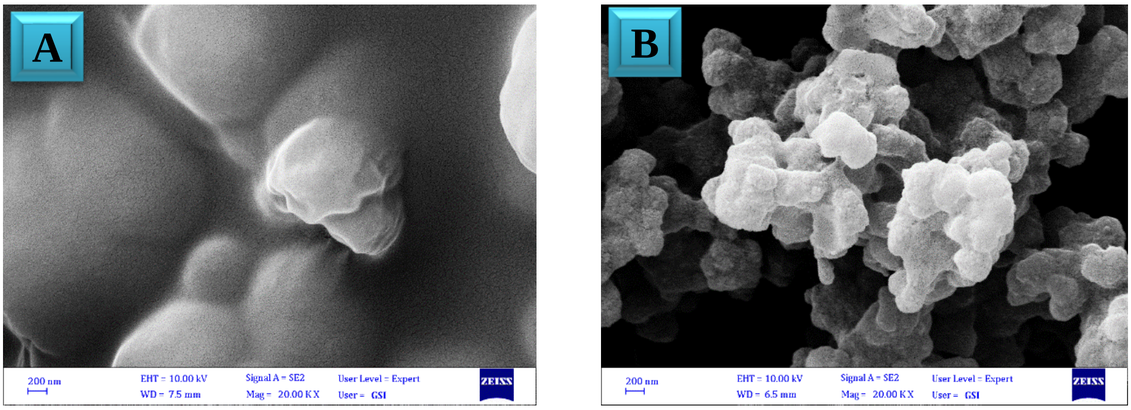


Fig. (4): SEM of Ca-IIP2
A. before the Ca ion was removed B. after the Ca ion has been removed

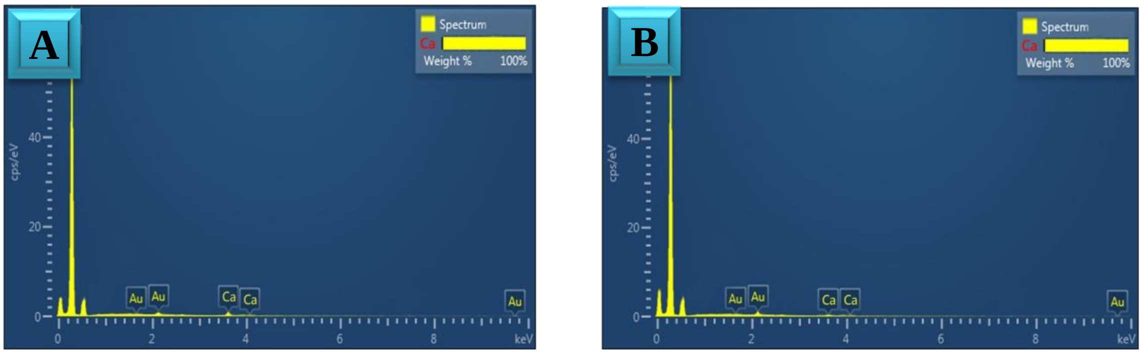


Fig. (5): EDX spectrum of Ca-IIP1
A. before the Ca ion was removed B. after the Ca ion has been removed

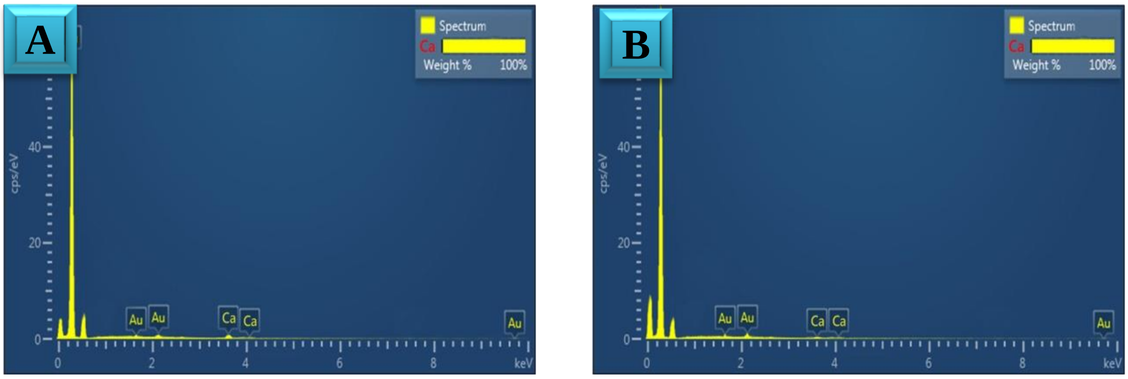


Fig. (6): EDX spectrum of Ca-IIP2
A. before the Ca ion was removed B. after the Ca ion has been removed

3.2. The optimum ratio of materials

The best ratios of calcium (II) ion, monomer, and cross-linker for creating molecularly imprinted and non-imprinted polymers were determined through a number of studies. The appropriate ratios for producing MIPs and NIPs with the best performance characteristics are shown in Table (3).

Table (3): Templet, monomer, crosslinker, and solvent variation ratios in the preparation of Ca- IIPs and NIPs

NO.	Ratio	salt $CaCl_2$	Styrene	EGDMA	Initiator	Solvent	Result
IIP1	% mmole	31.25 9.00	33.37 9.61	35.07 10.10	0.3 0.3	**5mL CH_3OH**	**Bottom-level salt precipitation**
IIP1	% mmole	4.81 1	46.26 9.61	48.62 10.10	0.3 0.3	**5mL CH_3OH**	**fluffy white gel**
IIP1	% mmole	1.73 1	32.72 20.0	65.25 40.0	0.3 0.3	**5mL CH_3OH**	**rigid white**
NIP1	% mmole	------ ------	33.23 9.61	66.46 19.22	0.3 0.3	**5mL CH_3OH**	**rigid white**
		salt $CaCl_2$	**1-vinyl imidazole**	**EGDMA**	**Initiator**	**Solvent**	**Result**
IIP2	% mmole	30.18 9.00	35.64 10.63	33.87 10.10	0.3 0.3	**5mL CH_3OH**	**Bottom-level salt precipitation**
IIP2	% mmole	4.58 1	48.77 10.63	46.34 10.10	0.3 0.3	**5mL CH_3OH**	**fluffy white gel**
IIP2	% mmole	1.73 1	32.62 20.0	65.25 40.0	0.3 0.3	**5mL CH_3OH**	**rigid white**
NIP2	% mmole	------ ------	33.23 9.61	66.46 19.22	0.3 0.3	**5mL CH_3OH**	**rigid white**

3.3 Adsorption condition

3.3.1. Adsorption time

The rate of absorption is a crucial consideration when using IIPs that have been created. Figures (7 A, and B) illustrate the outcomes for two IIPs from a study on variations in adsorption capacity concerning adsorption duration (1, 3, 5, 10, 30, 60, and 120 min). The Ca ion adsorption process in an aqueous solution containing Ca-IIPs is highly rapid at the beginning, as seen by the substantial rise in adsorption capacity in the first five minutes. The adsorption capacity then marginally rises when the adsorption time is extended from 5 to 10 minutes before remaining constant after 10 minutes. According to adsorption kinetics, Ca-IIPs are formed with binding sites that have a high affinity for Calcium ions, leading to high adsorption efficiency.

3.3.2. Adsorption capacity

Use the following equation to evaluate the adsorption performance of Ca-IIPs and to analyze the impact of the initial calcium ion concentration, which ranges from (0.25) to (15) mol/mL, on the adsorption capacity.

$$Q = \frac{(C_i - C_f)V_S * 1000}{M_{MIP}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where V_s is the volume of solution tested (ml), Q is the binding capacity of MIPs (mol/g), C_f is the final calcium(II) concentration (mol/ml), C_i is the initial calcium(II) concentration (mol/ml), and MMIP is the mass of dried polymer (mg).

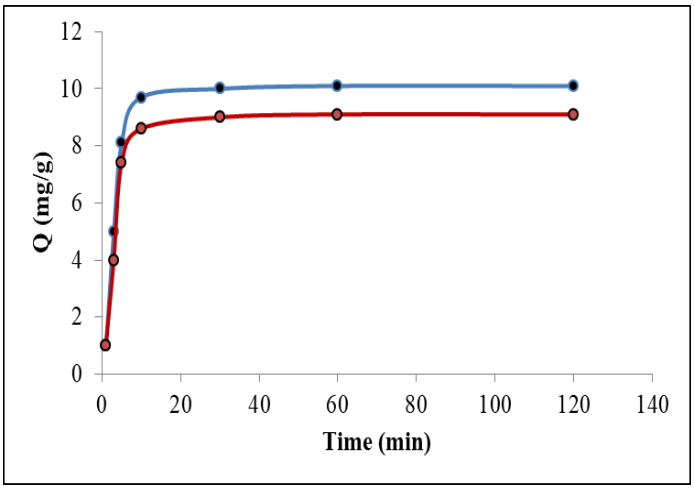


Fig. (7): Adsorption capacity changes that are time-dependent (100 mg IIPs, 20 mL of a 50 mg/L calcium solution, and 25°C). A. Calcium-IIP1, B. Calcium-IIP2

According to Fig. 8, when the concentration of calcium (II) ions rises, the adsorption capacity first rises quickly and then gradually. When the initial calcium (II) ion concentration rises, the mass transfer driving force is due to an increase in the differential between the concentration of calcium (II) ions in bulk solution and at the surface of IIPs, which significantly boosts the equilibrium adsorption capacity. However, the quantity of adsorbed metal remains constant when the concentration of calcium (II) is greater than 12.5 mol/ml.

The adsorption capacities of calcium -IIP1 and calcium -IIP2 are displayed in Tables (4,5), respectively. To determine the maximum adsorption capacity of calcium-IIPs, Langmuir isotherm models may be applied. as seen in Figure (9).

For Calcium -IIP1 and Calcium -IIP2, the highest adsorption capacity is (272.66) mol/g and (222.15) mol/g, respectively. The calcium-IIPs created in this work have a significant capability for adsorption. The produced Ca(II)-IIPs' ability to adsorb calcium(II) ions is significantly improved by the uniform and accessible imprinted binding sites. Additionally, the interaction between monomers and calcium(II) is quite stable, making the synthesis of chelation easy. The following illustrates the Langmuir adsorption isotherm equation.

$$\frac{Q}{C_{free}} = \frac{Q_{max} - Q}{K_d} \text{......................(2)}$$

where C_{free} is the free analytical concentration at equilibrium (mol/L), Q is the binding capacity, Qmax is the maximal apparent binding capacity, Kd is the dissociation constant at the binding site, and Cfree is the free analytical concentration. The equilibrium dissociation constant for a linear plot of Q/C_{free} vs. Q was calculated from the slopes (slop = -1/Kd), and the apparent maximum number of binding sites was calculated from the y-intercepts (intercept = Qmax/Kd) [21].

Table (4): View the conclusions of the Ca-IIP1 adsorption capacity studies along with their connection to the beginning concentration.

C_i* (μmol/mL)	***C_f* (μmol/mL)***	***Ci-C_f* (μmol/mL)***	***Q (μmol/g)***	***Q/C_f* (L/g)***
0.25	0	-	-	-
1.25	0	-	-	-
2.5	1	1.5	150	0.15
5	3.12	1.88	188	0.06
7.5	5.45	2.05	205	0.038
10	7.5	2.5	250	0.033
12.5	9.75	2.75	275	0.028
15	12.25	2.75	275	0.002

Table (5): View the conclusions of the Ca-IIP1 adsorption capacity studies along with their connection to the beginning concentration.

C_i (µmol/mL)	C_f (µmol/mL)	C_i-C_f (µmol/mL)	Q (µmol/g)	Q/C_f (L/g)
0.25	0	-	-	-
1.25	0	-	-	-
2.5	0.875	1.625	162	0.18
5	3.3	1.7	170	0.05
7.5	5.7	1.8	180	0.03
10	7.9	2.1	210	0.025
12.5	10.37	2.13	213	0.02
15	12.87	2.13	213	0.016

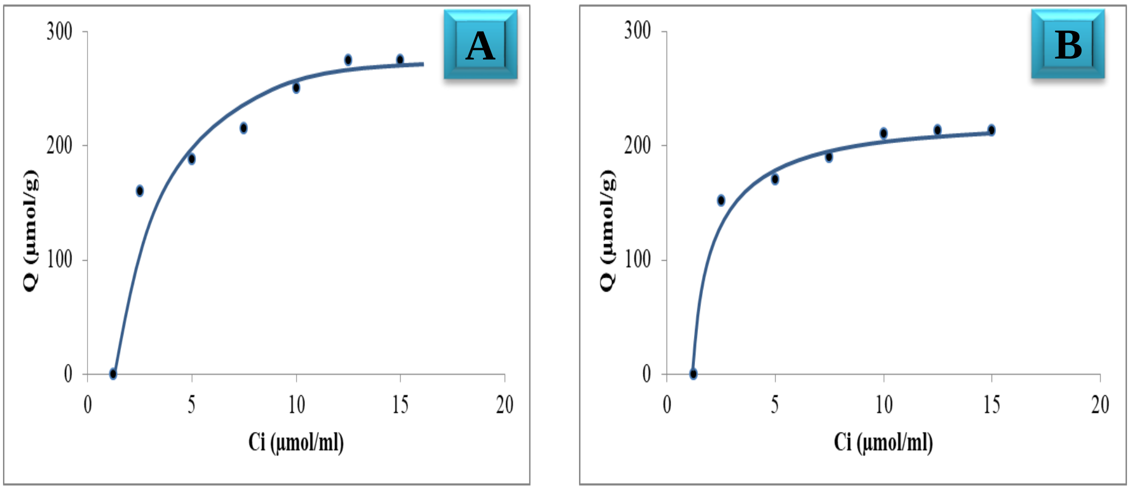


Fig. (8): The relation between the initial calcium ion concentration and adsorption capacit A. for Calcium-IIP1, B. for Calcium-IIP2

3.4. Application

3.4.1. Determination of Ca(II) ion in synthetic solution

A series of synthetic solutions was prepared to study the recovery of solid phase extraction-flame atomic absorption spectroscopy (SPE-FAAS) by using Calcium-IIPs Shown in Table (6).

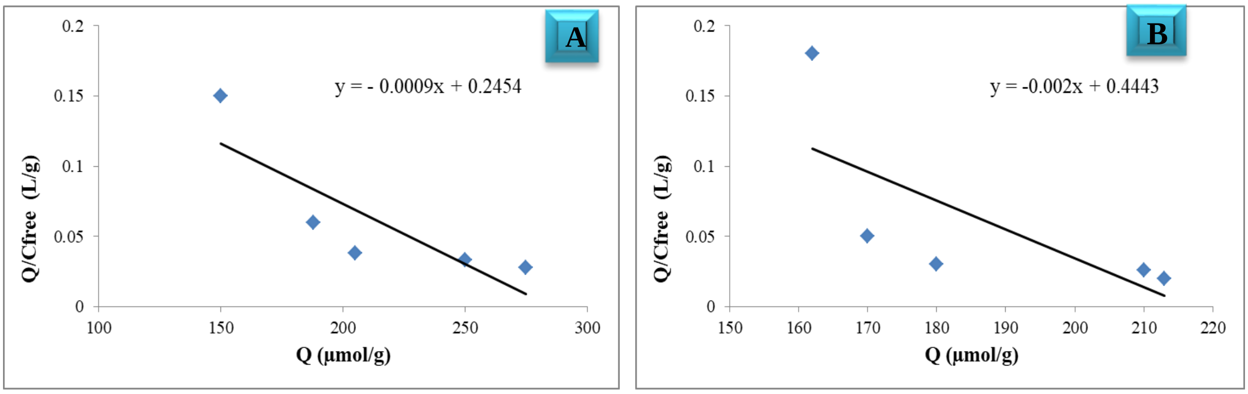


Fig. (9): Maximum adsorption capacity and the equilibrium dissociation constant are calculated using the connection between Q/Cfree (L/g) and adsorption capacity.
A. for Calcium-IIP1, B. for Calcium-IIP2

Table (6): Results of the determination of Calcium ions in aqueous synthetic solutions

NO.	Concentration Calcium ion (µg/mL)	Ca ion found (µg/mL) Using Ca-IIP1	Recovery %	Ca ion found (µg/mL) Using Ca-IIP2	Recovery %
1	1	0.98	98	1	100
2	5	4.9	99	4.8	98
3	10	10	100	9.9	99
4	20	20.0	100	20	100
5	30	29.5	98.3	29.7	99

3.4.2. Preconcentration in aqueous solution

Deionized water was used to prepare a 100 ml sample containing 5.0 ng/ml of calcium (II) ion, which was then injected into the calcium-IIPs SPE syringe at 1.0 ml/min. Air was blown through the column for five minutes after the sample loading. After 1mL of concentrated sulfuric acid was added, the calcium-IIP was allowed to sit in the tiny beaker for 8 minutes. Then 1ml of pure nitric acid is added, it is heated to 60 degrees, and 5ml of distilled water is added. The volume of the mixture is then immediately measured using a flame atomic absorption spectrophotometer. It is a concentration of 2–25 ng/mL, assuming we have a quantitative recovery. Tables (7) provide the characteristic performance data for the calcium-IIP1-SPE and preconcentration method. The relative standard deviation (n = 8) and the concentration of calcium ions in the sample (10 ng/mL) were used to assess the method's accuracy for a standard. Calculation of the detection limit.

Table (7): Preconcentration procedure performance characteristics for aqueous solution

Specification	**Ca-IIP1**	**Ca-IIP2**
Detection limit	10 ng/mL	10 ng/mL
Linear range	10- 25 ng/mL	10 - 25 ng/mL
precision	2.1	1.9
Equation of regression	AA = 7.081 C_V - 0.0002	

3.4.3. Determination of Calcium ion in refineries industrial water.

Before and after treatment, industrial water from refineries is analyzed to eliminate chemical components. These solutions were then injected into the Calcium-IIP-SPE packed column system in the same way as previously described after being filtered with a 0.5 m filter. Table (8) displays the outcomes as well as the recovery tests.

Table (8): Determination of Calcium ions in industrial water by Ca-IIP-SPE-AAS

Samples	**Ca-IIPs**	**Calcium ion add (μg.mL^{-1})**	**Calcium ion found (μg.mL^{-1})**	**Recovery (%)**
Industrial water (1) before treatment	Ca-IIP1	0.0	11.5 ± 0.8	-
		1.00	12 ± 1.4	96
		5.00	16.1 ± 0.9	97.5
		10.0	22 ± 1.2	102.3
Industrial water (2) before treatment	Ca-IIP2	0.0	15.5 ± 1.3	-
		1.00	16.2 ± 1.1	98.1
		5.00	26.4 ± 1.8	103.5
		10.0	26 ± 2.3	101.9
Samples		**Calcium ion add (ng/mL)**	**Calcium ion found (ng/mL)**	**Recovery (%)**
Industrial water (1) after treatment	Ca-IIP1	0.0	50.7 ± 2.1	-
		5.0	54.8 ± 0.8	98.3
		10.0	61.2 ± 2.1	100.8
		15.0	65.5 ± 1.5	99.6
Industrial water (2) after treatment	Ca-IIP2	0.0	55.4 ± 1.7	-
		50.0	105.5± 2.1	100.9
		100.0	155 ± 1.2	99.7
		150.0	206.8± 2.3	100.6

4. Conclusion

The creation of novel calcium-IIPs using bulk polymerization. EGDMA was used as the crosslinker, and the functional monomers styrene and 1-vinyl imidazole were chosen. In addition, benzyl peroxide was utilized as an initiator when chloroform was the solvent. The ideal dosages of the crosslinker and monomer for the calcium (II) ion were investigated. SEM allowed for the observation of the asymmetrical forms and three-dimensional network structure of polymers. Results from FT-IR and EDX demonstrated that the CH_3COOH/CH_3OH (3:30 v/v) solution successfully eluted Ca (II) ions. On adsorption efficiency, the effects of operation duration and starting Calcium (II) ion concentration were examined. Adsorption by IIPs occurred quickly (equilibrium was attained in less than 10 minutes), and it complied with Langmuir isotherm models. The maximal adsorption capacities of Calcium -IIP1 and Calcium -IIP2 are greater than those of other sorbents mentioned in the literature at (272.66) mol/g and (222.15) mol/g, respectively. The cavity structure and chemical characteristics of the polymers are mostly unaffected by the elution process, demonstrating the remarkable stability and regeneration abilities of calcium-IIPs.

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