

Article

## Rapid Development of Molecularly Imprinted Polymers for Efficient Removal of Cadmium Ions from Water

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**Abstract:** Molecularly imprinted polymers (MIPs) are specialized cross-linked polymer networks designed to show strong affinity for specific target molecules, ions, or metallic species with remarkable selectivity for structurally related compounds. This study reports the development of a cadmium (II) ion-imprinted polymer (Cd-IIP) designed for the selective extraction of Cd<sup>2+</sup> ions from aqueous solutions. The polymer was synthesized via bulk polymerization using 4-vinylpyridine as the functional monomer, and its structure and composition were thoroughly characterized using TGA, SEM, and CHNS elemental analysis. Adsorption experiments confirmed that the material exhibits high affinity for Cd<sup>2+</sup>, with kinetic data following a pseudo-first-order model and thermodynamic results indicating an exothermic adsorption process. When evaluated in binary metal-ion systems, the polymer demonstrated excellent selectivity. Additionally, throughout several adsorption-desorption cycles, the material demonstrated outstanding regeneration capability

**Keywords:** Molecularly imprinted polymers; metals; adsorption, Selectivity

### 1. Introduction

The rational design of polymer architectures that can precisely identify and bind target species is made possible by molecular imprinting technology. Cross-linked polymer matrices with a strong affinity for specific target molecules, ions, or metallic elements are known as molecularly imprinted

polymers (MIPs) (Priyadarshane & Das, 2021). MIPs have been widely used in many different scientific fields because of their distinct molecular recognition capabilities and predictable structural features (Liu et al., 2024, Ndunda, 2020). One particularly promising method for improving MIPs' recognition abilities is metal ion imprinting (Ansari et al., 2017). Through bioaccumulation in food chains, cadmium (Cd) is a highly toxic heavy metal that poses significant risks to biological systems and environmental health even at trace concentrations. Cadmium is one of the thirteen most hazardous metals listed by the EPA as a non-essential element (Cui et al., 2022). It has been shown to have detrimental effects on a number of physiological systems, including the cardiovascular, renal, neurological, gastrointestinal, reproductive, and respiratory systems (Kumar & Kumar, 2019, Wang et al., 2010). It is also a confirmed human carcinogen (Ahmed et al., 2025, Haddad et al., 2025). In order to assess the usefulness of MIPs for the selective identification and removal of cadmium ions from aqueous environments, the current study focuses on creating a Cd (II) ion-imprinted polymer. The produced MIPs demonstrated strong selectivity for the target metallic ion along with a significant binding capacity.

## 2. Research Methodology

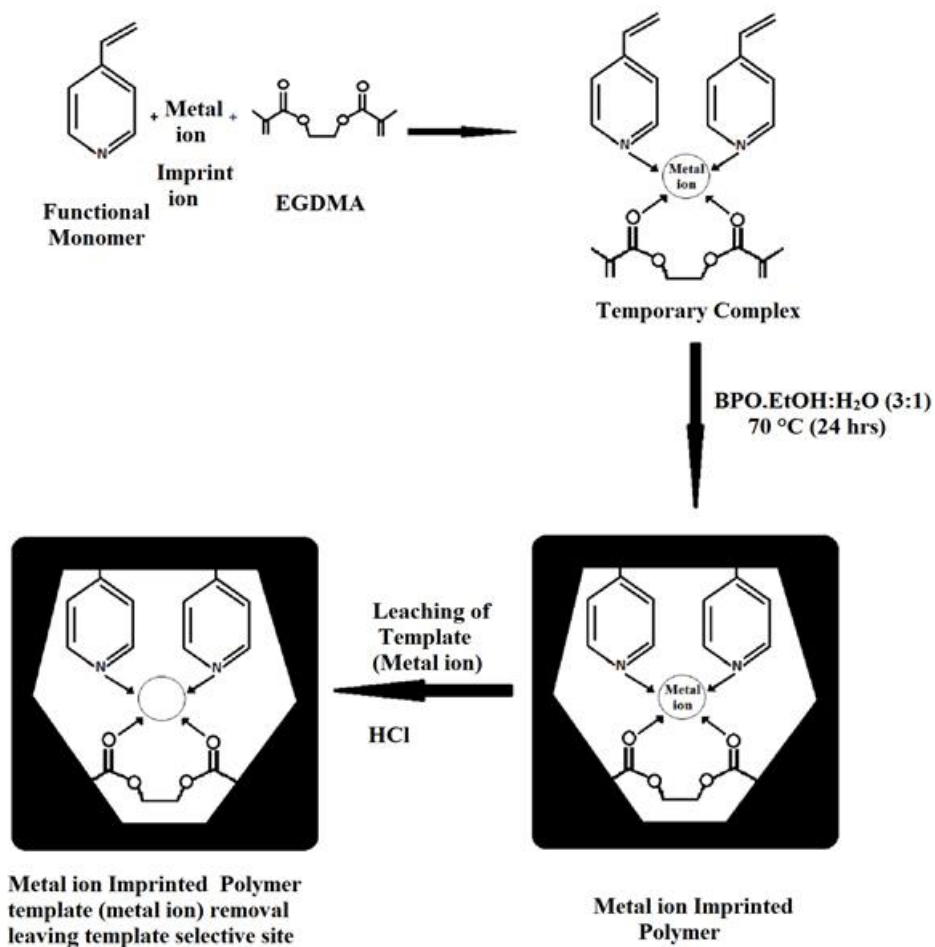
### 2.1 Materials

4-vinyl pyridine (4-VP) was purchased from ACROS Organics, New Jersey USA. Ethyleneglycol dimethacrylate (EGDMA), Benzoyl peroxide (BPO) was purchased from (Trade TCI mart) TCI-EP Tokyo Kasei Kogyo Co. Ltd, Japan. All other chemicals were reagent grade and purchased from ACROS Organics, New Jersey USA.

### 2.2 Synthesis of Cd (II) Ion Imprinted Polymer (IIP):

The fabrication of Cd (II) ion imprinted polymer was done by radical polymerization by dissolving (4 mmol) of  $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in a (3:1) mixture of ethanol: water followed by addition of (12 mmol) of 4-vinyl pyridine (VP), (60 mmol) of ethyleneglycol dimethacrylate acid (EGDMA) and 10 mg of benzoyl peroxide (BPO). The reaction mixture was further exposed to sonication for 1 hour. After purging with  $\text{N}_2$  for 10 min polymerization reaction was initiated by placing reaction tube in oven at 70 °C for 24 hours. Finally, the prepared polymer was removed from reaction tube and washed with ethanol and deionized water to eradicate, unreacted monomer. The crushed and sieved polymeric product was treated with 0.5 M hydrochloric acid to eliminate the template ion. The same step was repeated frequent times till the template ion was hundred percent removed followed by washing with methanol to remove extra amount of HCl. After removal of template a cavity is produced in polymer matrix that is responsible for adsorption of Cd ions from aqueous solution. The fabricated MIP product was employed to eliminate Cd (II) ions from aqueous solution. The mechanism of MIP synthesis is given in Fig. 1. The non-imprinted

polymer (NIP) was also prepared by similar procedure in the absence of template Cd ion.



**Figure 1:** Schematic representation of synthesized Cd (III) ion Imprinted Polymers

### 2.3 Batch Adsorption Experiment

To explore the adsorption performance of Cd (II) ions, the batch mode of adsorption was applied by optimizing pH, the dose of adsorbent, rpm,

concentration and shaking time. The % Adsorption Capability was calculated using this formula:

$$\%Adsorption = (C_i - C_e) / C_i \times 100 \dots \dots (1)$$

Where  $C_i$  is the initial concentration &  $C_e$  is the concentration at equilibrium in (mol/dm<sup>3</sup>), The initial and equilibrium concentrations were determined by atomic absorption spectroscopy.

Sample	C	H	N	S
IIP-Cd (II)	60.95 %	5.99 %	9.48 %	0
NIP	61.29 %	6.71 %	9.37 %	0

### 3. Results

#### 3.1 Characterization of Cd (III) ion imprinted polymer

##### 3.1.1 CHNS Analysis:

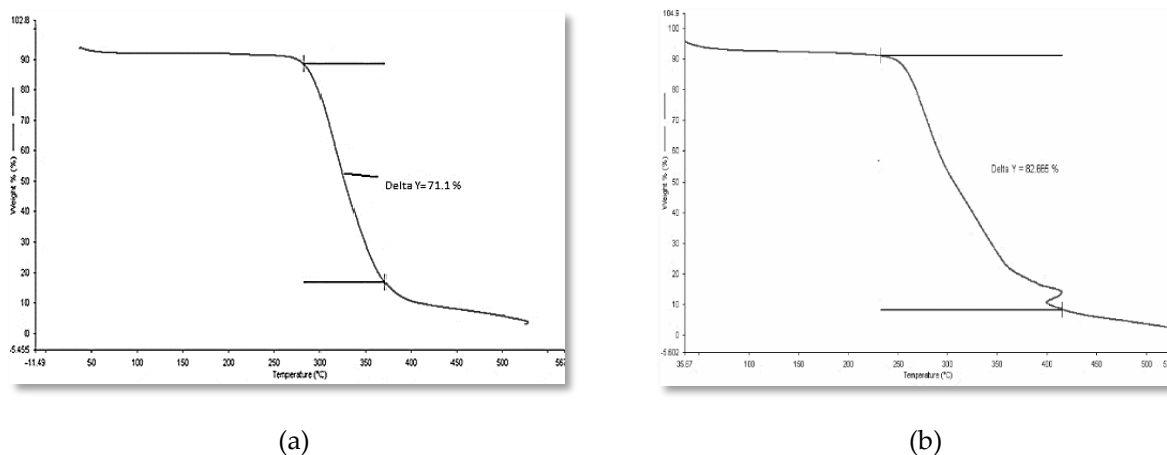
The CHNS elemental analysis of prepared molecularly imprinted polymer (MIP) was done by using CHNS Analyser FLASH THERMO EA. 1112 series and outcomes of examination are presented in table 1.

**Table 1.** CHNS analysis of synthesized ion imprinted polymer (IIP).

##### 3.1.2 Thermogravimetry (TG)

Thermal stability of the Cd (II) ion imprinted polymer (IIP) was checked by Perkin Elmer's Diamond TG Thermal Analyzer through Pyris Manager

Software by performing thermo gravimetric analysis (TGA) as shown in figure 2 (a) for NIP & (b) for Cd (II)IP. The thermo gravimetric examination (TGA) exhibited complete great stability of fabricated MIPs and results are exhibited in table 2.



**Figure 2:** Thermo Gravimetric Analysis of NIP & Cd (II) Ion Imprinted Polymer

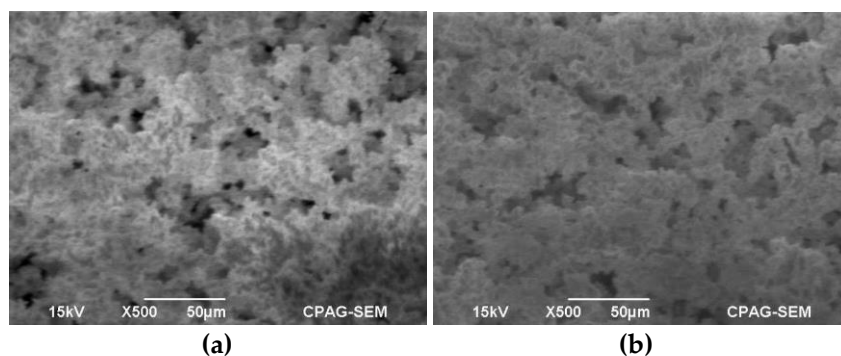
**Table 2.** Thermo gravimetric analysis of synthesized ion imprinted polymer

Sample	TGA Characteristics			Possible Molecular Involvement
	1 <sup>st</sup> Stage Weight Loss	2 <sup>nd</sup> Stage Weight Loss	3 <sup>rd</sup> Stage Weight Loss	
IIP-Cd (II)	36-225 °C (9 %)	225-420 °C (82.665 %)	400-525 °C (10 %)	1 <sup>st</sup> weight loss indicates the removal of solvent. 2 <sup>nd</sup> weight loss is due to organic part of polymer. 3 <sup>rd</sup> weight loss is owing to metal oxide residue.

NIP	40-260 °C (10 %)	260-365 °C (71.1 %)	365-540 °C	1 <sup>st</sup> weight loss is due to solvent interaction. 2 <sup>nd</sup> weight loss represents organic part of polymer.
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### 3.1.3 SEM Analysis:

The (SEM) analysis is used to approve structural reliability of fabricated ion imprinted polymers (Cormack & Elorza, 2024). In current study, the scanning electron microscopic images were done using JEOL/EOJSM-6490 scanning electron microscope and the results are shown in figure 3(a) & 3(b). The surface morphology of Cd (II)-IIP & NIP evidently revealed the synthesized polymers having high roughness and porosity.



**Figure 3:** SEM image of (a) Cd (II)-IIP & (b) NIP

### 3.2 Equilibrium Studies

In adsorption studies the adsorption isotherms have a significant role in predicting demonstrating of adsorption systems. Freundlich adsorption isotherm is used to describe the exponential distribution of sites, heterogeneity of the surfaces and their energies. Freundlich (Eq. No.2) and Langmuir (Eq. No. 3) isotherms have been used to analyse the equilibrium experimental data.

$$\log C_{ads} = K_F + \frac{1}{n} \log C_e \dots \dots (2)$$

$$\frac{C_e}{C_{ads}} = \frac{1}{K_L} b + \frac{C_e}{K_L} \dots \dots (3)$$

### 3.3 Kinetic Studies

The kinetic study of the adsorption is calculated by using the pseudo first- order equation as

$$\ln (q_e - q_t) = \ln q_e - kt \dots \dots (4)$$

### 3.4 Thermodynamic Studies

In thermodynamic studies following equations is used to calculate the activation parameters like  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ .

$$\ln Kc = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \dots \dots (5)$$

$$\Delta G = \Delta H - T\Delta S \dots \dots (6)$$

## 4. Discussions

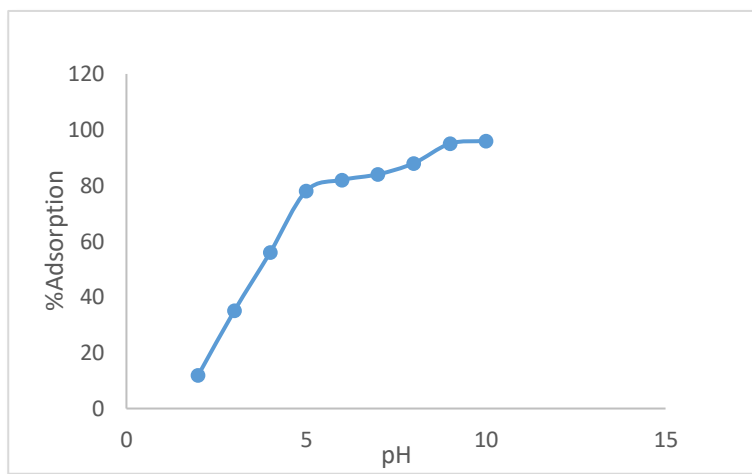
### 4.1 Removal of Cd (II) by Ion Imprinted Polymer (IIP)

The synthesized Cd (II) - (IIP) was utilized to remove imprinted metal ions from aqueous media by optimizing diverse experimental environments.

#### 4.1.1 Effect of pH

The pH of medium has an imperative role during adsorption studies. The adsorption examination for Cd (II) was done over the range of pH 2-10 by taking 5 mg of polymer with 10 ml of 5 ppm salt solution at shaking speed of 100 rpm for 30 min at room temperature. It was perceived that with the rise of pH the % adsorption was increased as visible in figure 4, the maximum efficiency was observed at 9 pH. At lower limits of pH, the binding groups present in template specific sites were protonated as a result of increase in hydrogen ion concentration increase in H<sup>+</sup> ion concentration. In acidic pH, the lower extent of adsorption rate confirmed that the hydrogen ions are the competitor ions of imprinted ions and

nitrogen of pyridine groups on polymer surface is accountable for the attachment of Cd (II) (Luo et al., 2011, Guo et al., 2014).

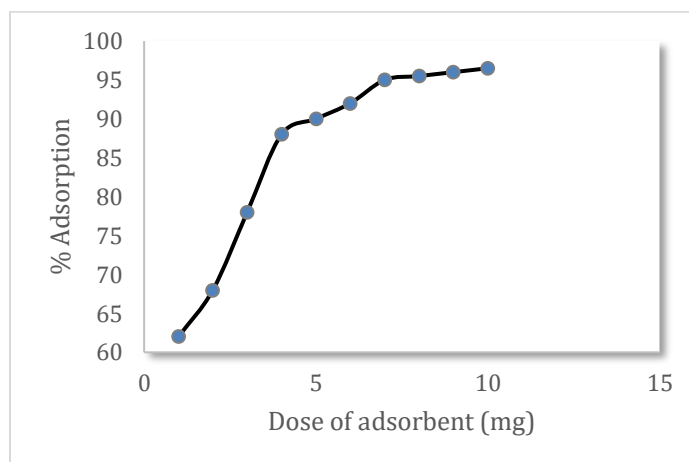


**Figure 4.** pH effect on adsorption of Cd (II) onto an ion imprinted polymer

#### 4.1.1 Effect of Adsorbent Amount

Another topmost major factor accountable for adsorption competence is amount of MIP for adsorption of Cd ions at a given initial concentration (Memon et al., 2007& 2009). Studies on effect of adsorbent amount for the elimination of Cd (II) ion was done by changing the amount of adsorbent from 0.001-0.01 g per 10 ml of 5 ppm salt solution. As presented in figure. 5 the % adsorption increases till 0.005 g, and after that there is no significant change was observed. This shows that at certain concentration of adsorbent % adsorption increases and after that it shows no major change due to saturation of vacant sites and fixed amount of adsorbate. After 0.007 g of adsorbent no significant increase was observed in % adsorption

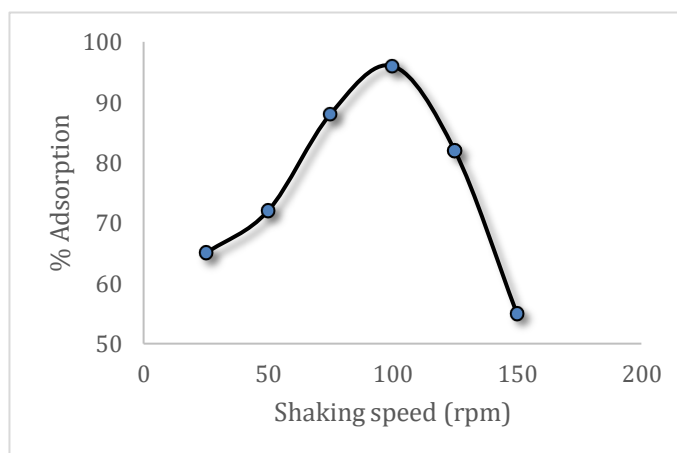




**Figure 5:** Adsorbent Amount effects on adsorption of Cd (II) onto ion imprinted polymer (II)

#### 4.1.3 Effect of Shaking Speed

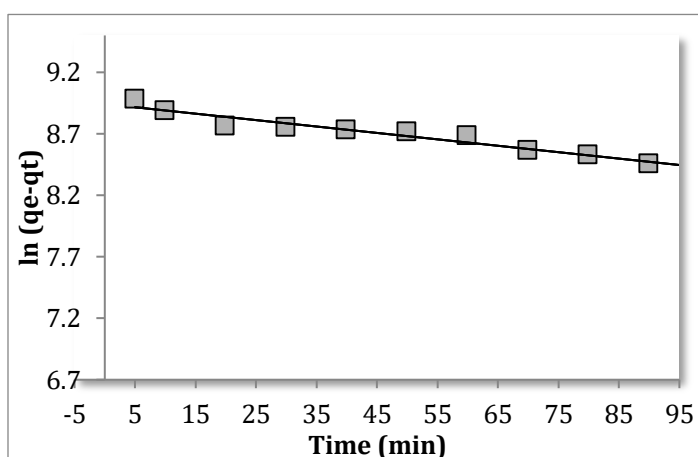
The adsorption capability is depending on another important parameter i.e., shaking speed for the adsorption of metal ions (Zhang et al., 2012). On the adsorption of Cd (II) the influence of shaking speed was observed from 25-150 rpm. As revealed in figure. 6 it was observed that with increase in shaking speed the % adsorption increases till 100 rpm after that a decrease was seen with increasing shaking speed. So, the 100-rpm shaking speed was used for more studies on individual metal ions.



**Figure 6:** shaking speed effect on adsorption of Cd (II) onto an ion imprinted polymer

## 4.2. Kinetics of Adsorption

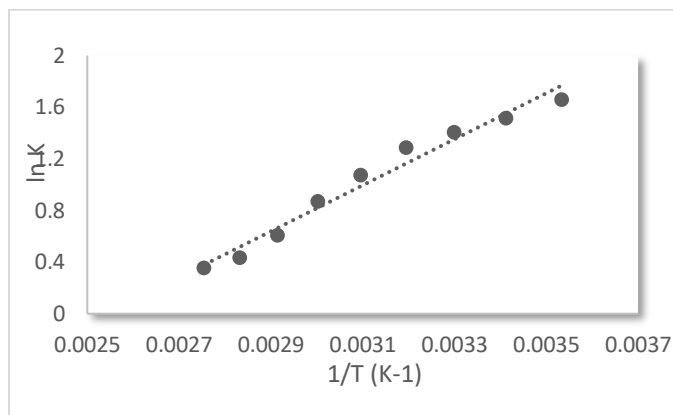
The time for completion of adsorption reaction was determined in a batch experiment by shaking 5 mg of adsorbent in metal salt solution of preferred concentration for 5-100 minutes at previously optimized adsorption parameters i.e. 9 pH, 30 °C temperature etc. It was observed that % adsorption increases till 30 min and after that there is no major change was observed (Qiu et al., 2009). The adsorption process followed pseudo 1st order rate equation as shown in Fig. 7. The rate constant was calculated as 0.011min<sup>-1</sup> with R<sup>2</sup> 0.932 using Lagergren equation.



**Figure 7:** Kinetic studies for the adsorption of Cd (II) onto an ion imprinted polymer (IIP)

## 4.3 Thermodynamic studies

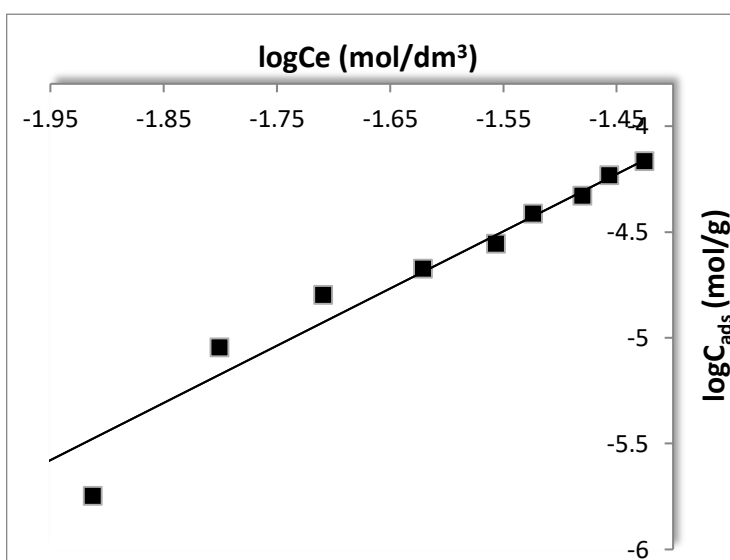
For studying consequence of temperature on Cd (II) ions adsorption by an ion imprinted polymer was carried out in the temperature range of 283-363 K, at 9 pH, for 30 min of shaking time. The maximum efficiency was observed at low temperature and was decreased at high temperature this reveals exothermic and spontaneous nature of adsorption process with  $\Delta H$  -20.9 kJmol<sup>-1</sup>,  $\Delta S$  -5.3 kJmol<sup>-1</sup>,  $\Delta S$  -0.054 kJmol<sup>-1</sup>K<sup>-1</sup> and R<sup>2</sup> 0.93, shown in figure 8.



**Figure 8:** Thermodynamic studies for the adsorption of Cd (II) onto an ion imprinted polymer (IIP)

#### 4.4 Equilibrium Studies:

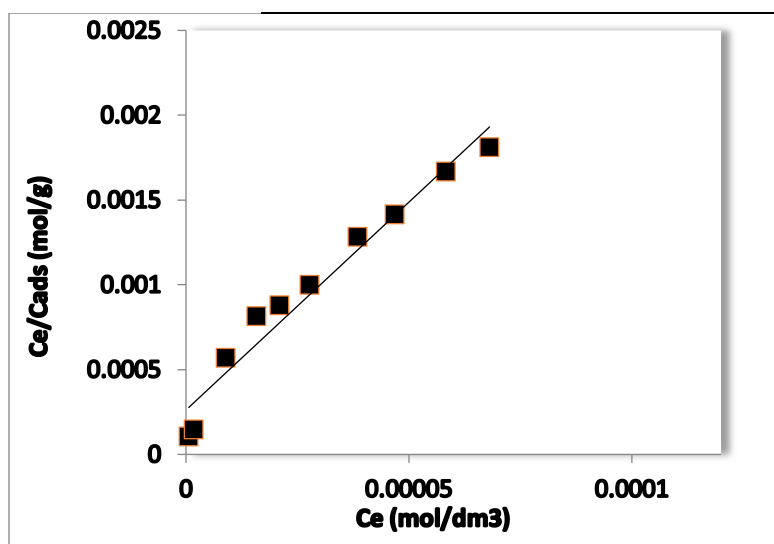
Adsorption studies were performed by applying Langmuir and Freundlich model. The adsorption data is well fitted to both Langmuir and Freundlich models as shown in 9 and 10. The monolayer and multilayer adsorption capacities along with R<sup>2</sup> and other constant parameters are mentioned in Table 3.



**Figure 9:** Freundlich adsorption isotherm for removal of Cd ions from aqueous solution

**Table 3.** Adsorption isotherm parameters for Zn (II) & Cd (II) Ion Imprinted Polymers

Adsorption isotherms	Isotherm parameters	Cd (II)
Freundlich isotherm constants	$1/n$	$0.359 \pm 0.02$
	$K_F$ (mmol/g)	$1.158 \pm 0.12$
	$R^2$	$0.971 \pm 0.003$
Langmuir isotherm constants	$K_L$ (mmol/g)	$0.040 \pm 0.005$
	$b$ (dm <sup>3</sup> /mol)	$8173 \pm 2.9$
	$R_L$	$0.430 - 0.070$
	$R^2$	$0.960 \pm 0.003$

**Figure 10:** Langmuir adsorption isotherm for removal of Cd ions from aqueous solutions

#### 4.5. Selectivity Studies:

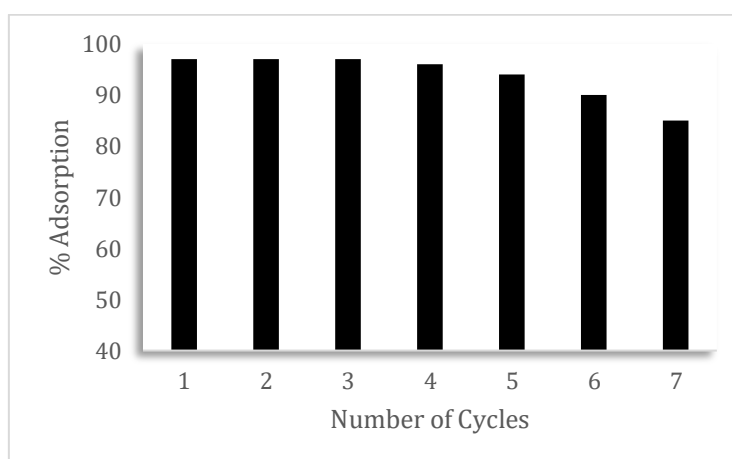
In order to examine the specificity of both synthesized Cd (II) ion imprinted polymer for their respective metal ions competitive adsorption of other similar metal ions were studied. The comparative study for Pb (II) & Al (III) was done via preparing Cd (II)/ Pb (II) & Cd (II)/Al (III) binary mixed solutions of similar concentration for both metal ions. Adsorption study was done by using this mixed solution in batch method. The selectivity of metal ion depends on the ionic radius and oxidation state of comparative metals. The ionic radius of imprinted metal ion Cd (II) = 95 pm smaller than Pb (II) = 119 pm , and Al has larger oxidation state with smaller ionic radius of 53.5 pm. The distribution coefficients ( $K_d$ ), and selectivity coefficient  $k$  ( $k = K_d$  of template ion/ $k_d$  of comparative ion) of comparative selectivity study are summarized in Table 4 which revealed that selective adsorption potential for imprinted metal ion Cd (II) by Cd (II) – IIP confirmed by decrease in  $K_d$  &  $k$  values of comparative metal.

**Table 4. Parameters of selectivity studies for Cd (II) Ion Imprinted polymer**

Metal ion	$K_d$	$K$
Cd (II)	3.8	--
Pb (II)	1.12	3.39
Al (III)	1.26	2.9

#### 4.6. Desorption and Regeneration Studies

The economic achievement of adsorption evolution be liable upon adsorbent reusability, consequently desorption and regeneration study is very significant (Fan et al., 2012). In present study the reusability of synthesized Cd (II) – IIP was tested by repeating adsorption- desorption cycles for seven times by using same adsorbent. The effect of reusability as shown in figure 11 displayed minor decrease of almost 15 % for Cd (II) – IIP in adsorption capability of adsorbent after seven repeated cycles. The results revealed that the synthesized ion imprinted polymers can successfully be reutilized for further applications.



**Figure 11:** The effect of reusability of Cd (II) Ion imprinted polymer for adsorption of Cd (II) ions

#### 4.7 Analytical applications to water samples

The synthesized ion imprinted polymers (IIP's) was used to remove Cd ions from environmental water samples. Water samples were taken from industrial areas of district Sadiqabad & Rahim Yar Khan. Total number of six samples was collected of which three of ground water and three of surface water. The collected samples were filtered to remove particulars. The adsorption study of metal ions was done by spiking procedure by preparing 10 ppm Cd (II) solution in real water samples and

in deionized water. The atomic absorption absorbance measurements were done for spiking samples and for metal ion solution in deionized water and the amount of metal ion in real sample were estimated as (table 5).

**Table 5** Removal of Cd ions from environmental water samples using Cd (II) ion imprinted polymer

Samples	Determined Amount of metal ion in ( $\mu\text{g/L}$ )		Adsorption (%)
Abbasia town (RYK)	Cd (II)	2.45	$90.0 \pm 1.0$
Gulshan-e-Arjumand (RYK)	Cd (II)	2.11	$89.0 \pm 1.2$
Canal road (RYK)	Cd (II)	1.85	$98.0 \pm 0.7$
Link road (SDK)	Cd (II)	2.90	$90.0 \pm 1.2$
Mantaqabad (SDK)	Cd (II)	1.99	$91.0 \pm 0.5$
Mukhtargarh (SDK)	Cd (II)	2.81	$88.0 \pm 1.4$

## 5. Conclusions

Molecularly imprinted polymers (MIP's) are exceptionally crossed linked and extremely specific in nature for binding certain marks. The current work explored the fabrication of ion imprinted polymers (IIP) with efficient removal capability for targeted metal ions from aqueous solutions and environmental samples. The removal parameters were standardized in 30 min as the adsorption was equally fast due to geometric desirability between metal ions and template hollows in the polymer matrix. The selectivity and reusability study for fabricated ion imprinted polymers (IIP's) demonstrates great selectivity to template metal ions in presence of other competitor metal ions and can be reusable without misplacing adsorption ability.

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### Competing Interests

The authors have no competing interests to declare that are relevant to the content of this article.

### Data, Materials, and Code Availability

The datasets generated and/or analysed during this study are available from the corresponding author upon reasonable request.

### Authors' Contributions

All authors contributed equally to the conception, development, and writing of this manuscript and have approved the final version for submission.

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