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Synthesis of Molecularly Imprinted Polymer for the Selective Removal of Mercury

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ABSTRACT

An adsorbent consisting of Hg^{2+} ion imprinted polymer (IIP) was prepared and used for removal of Hg^{2+} from real water samples. IIP was synthesized by utilizing 1-vinylimmidazole and methacrylic acid as complexing agent and monomer. IIP was characterized by FT-IR, SEM and EDX to investigate the functionality, morphology and elemental analysis. Adsorption isotherms and kinetics of Hg^{2+} ion on Hg^{2+} imprinted polymer have been studied and adsorption phenomenon of IIP was found to follow the Langmuir isotherm and pseudo second order kinetic model. Other parameters such as pH, temperature, shaking speed, and agitation time affecting the adsorption of Hg^{2+} were also optimized. The relative selectivity coefficient of imprinted polymer for Hg^{2+} / Cu^{2+}, Hg^{2+} / Cr^{3+}, Hg^{2+} /Co^{2+} were 122, 103, 76, respectively.

Keywords: imprinted polymer, Hg^{2+}, selective recognition, adsorption, toxicity, drinking water

INTRODUCTION

Mercury is a toxic element which exists in the natural environment; it is a constituent of earth's crust and is present in aquatic sediments, soil, water, air, animals and living plants [1]. Nearly 3400 metric tons of elemental mercury is released into global environment per year and approximately 95% remains in terrestrial soil, 3% in surface ocean water, and 2% in the atmosphere. Around 70% of the mercury pollutant comes in the environment through anthropogenic sources [24]. Mercury is a harmful pollutant in the biosphere and considered to be a human health hazard. When it enters the body, it binds with sulfhydryl groups to inactivate key enzymes responsible for preventing oxidative damage and causes symptoms of neurological damage, kidney and liver toxicity [2,3,4,5].

Production of mercury-containing products is progressively increasing; it is essential in manufacturing of thermometers, batteries, cathode tubes, cameras, medical laboratory chemicals and equipment, and has been used as a catalyst in the production of urethane polymers for plastics, a cathode in the production of chlorine mercury vapor lamps and barometers. Hence, monitoring mercury level in environment is very much essential [6].

To clear the aqueous environment of mercury contamination, many pre-concentration and separation methods are stated; photo-catalysis [7], biological processing [8], Solid Phase Extraction (SPE), Cloud Point Extraction (CPE), solid and liquid phase micro extraction [9] ion exchange precipitation, co-precipitation, chemical precipitation [10] complexation, flotation [11], coagulation, electrodeposition and membrane filtration [12], electrochemical [13] bio-filtration [14] electrolysis and cementation [15].

Hence, selectivity is a requiring consequence and it is hard to accomplish with methods and materials defined earlier. To deal with the alarming problem and to get better selectivity, Molecular Imprinted Polymer (MIP) has

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been synthesized. MIP's have recognition characteristics [16] with non-covalent approach. In MIP's, a template molecule interacts with a functional monomer and a crosslinker in a porogen solvent [17] and after successful polymerization, the removal of the template generates the recognition cavities inside the three-dimensional copolymer network. Nishidi in 1976 introduced Ion Imprinted Polymers (IIP's) similar to MIP's differ only by template molecule which is metal ion in IIP's [18].

In this study, Hg^{2+} ion imprinted polymer (IIP) is synthesized by precipitation copolymerization by utilizing methacrylic acid (MAA) as a monomer, 1-vinylimmidazole as a specific ligand for Hg^{2+} ions andethylene glycol dimethacrylate (EGDMA) as a cross-linker.Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), and Electron Diffraction X-ray (EDX) were used for the characterization. Factors affecting the separation were studied and optimized pH of solutions, desorption, and sorption rate.

EXPERIMENTAL SETUP

Materials

Methacrylic acid (MAA), ethyleneglycoldimethacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), 1-vinylimidazole were obtained from Aldrich (USA), Mercuric chloride ($HgCl_2$), and methanol and other chemicals were obtained from Merck, Germany.

Instrumentation

A Flame Atomic Absorption Spectrophotometer (FAAS) (Perkin-Elmer Model Analyst 700, Norwalk, CT) was used for the determination of selected metals. To acquire maximum absorbance signal, adjustments in the acetylene flow rate and the burner height were made. pH meter, a Metrohm 781 pH meter was used for pH adjustments. Milli-Q machine and ultrapure (Milli-Q) water were obtained from Milli-Q water purification machine (Elga Co. USA.) Utrasonicator, electronic balances, magnetic Stirrer and heating instruments were used during all experiments work.

Synthesis of Hg^{2+} Imprinted Polymer

Hg^{2+} ion imprinted polymer was prepared via thermal precipitation polymerization technique.1.5mmol of $HgCl_2$, and 6.0mmol of 1-vinylimmidazole 6.0mmol of MAA were dissolved in 10mL of methanol and sonicated for 30 minute for complexation, then 30mmol of EGDMA and 0.009g of AIBN were dissolved 10mL of methanol and added in a 50mL reaction flask. Polymerization was performed at 60^{o}C with for next 18 hours under nitrogen environment. Non-imprinted polymer was also prepared through same procedure without template (Hg^{2+} ions). Afterwards IIP and NIP were washed with MeOH:H_2O repeatedly to remove un-reacted materials.

Leaching of the Hg^{2+} Ions from Imprinted Polymer

Hg^{2+} ion imprinted polymer stirred for 30 minutes in 1M HCl, and the method was repeated 5 times to accomplish leaching of Hg^{2+} ions, than, washed with D.I water until neutral pH was achieved. Then, the polymer was dried in vacuum oven at 70^{o}C.

RESULTS AND DISCUSSION

Characterization of the Hg^{2+}-Imprinted Polymer

Scanning Electron Microscopy (SEM)

Surface and morphology investigation of the synthesized IIP's were done by using back-scatter detector. **Figure 3** shows the difference between the SEM images of IIP's. NIP (A) has uniform and smooth surface, while at another hand SEM image of IIP (B) exhibits a fractured and irregular surface due to the imprinting of Hg^{2+} ions in polymeric material, and in contrast to NIP and IIP, the polymer after leaching of Hg^{+2} ions(C) possesses porosity in the polymeric material which facilitates the binding of the template ions.

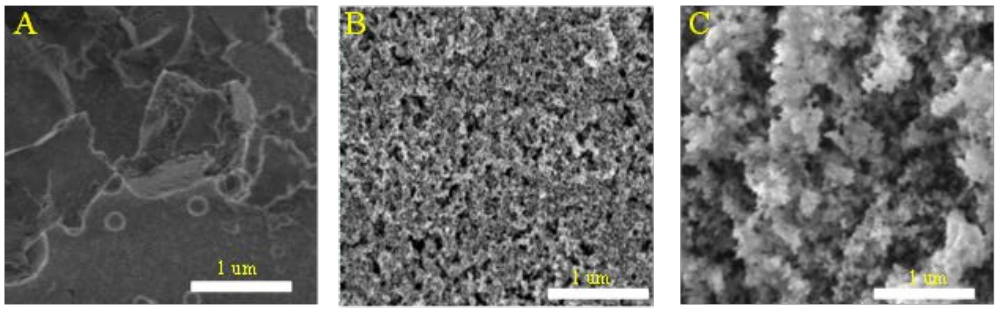

Figure 1. SEM images for (A) NIP (B) IIP(C) IIP after the leaching o

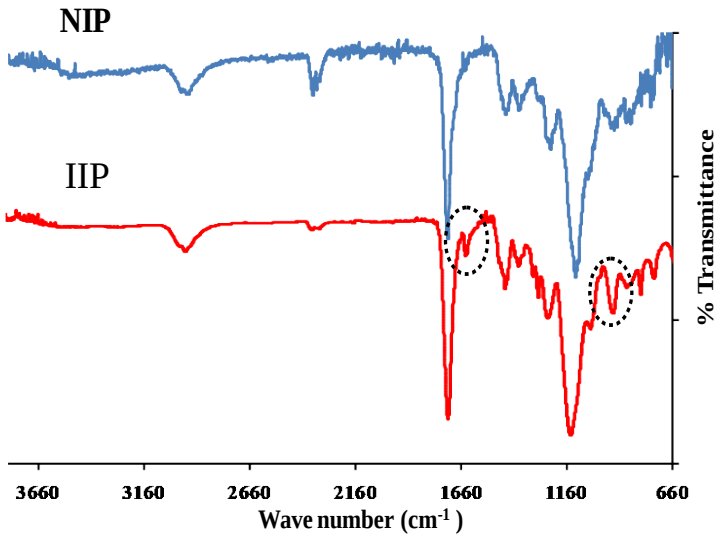

Figure 2. FT-IR (blue line) NIP and (red line) I

Fourier Transform Infrared spectroscopy

In order to ascertain the imprinting of Hg^{2+} ions in polymer matrix, the FT-IR analysis were carried out by using KBr pellet method. **Figure 2** shows the FT-IR spectra of both NIP and Hg-IP, the similarity between these IR spectra means that both the polymers have same backbone [25]. The peak at 911 cm^{-1}in fingerprint region is characteristic for the Hg^{2+} ion and, other peak observed at 1600 cm^{-1} in (**Figure 2A**) Hg-IIP due to – C=C and C=N which is reduced in (**Figure 2B**) NIP spectra. This amount of reduction in band frequency is evidence for the coordination of the Hg^{2+}ions with non-bonding electron pairs of nitrogen in N-C group in 1-vinylimidazole. The peak at 1710 $cm^{-1}$is responsible for ester carbonyl group. The bands at 1160 cm^{-1}, 1200cm^{-1} were assigned to the asymmetric and symmetric modes of C-O-C bonds and C-C bonds in ester group, whereas, bands at 2960cm^{-1} and 2926cm^{-1} are accounts for the stretching vibration mode of the aliphatic C-H groups [19].

Energy-dispersive X-ray spectroscopy (EDX)

To confirm the formation of NIP, IIP, and presence and absence of Hg^{2+} ions after leaching from IIP, the elemental analysis was conducted by Energy-dispersive X-ray spectroscopy (EDX). **Figure 3A** NIP with three major peaks corresponds to O, C, and S and, there is no other signal which confirms the purity of polymer. The IIP shown in **Figure 3B** has an extra peak of Hg^{2+} ion in the spectrum which is the evidence for the successful imprinting of the Hg^{2+} ions. Absence of Hg^{2+} ions signal in **Figure 3C** EDX spectra of IIP after removal of template confirms the leaching of Hg^{2+} ions from polymeric material.

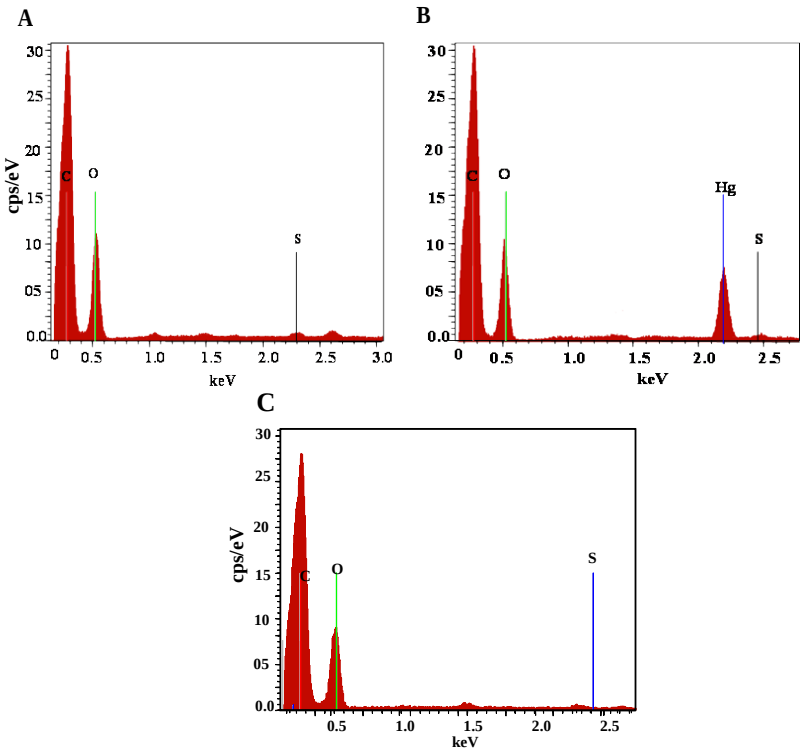

Figure 3. EDX spectra for (A) NIP (B) IIP (C) IIP after the leaching of Hg^{+2} ions

Adsorption of Hg^{+2} Ions on IIP

The containing power of IIP to adsorb Hg^{2+}ions were studied via batch experiment by equilibrating 20 mg of adsorbent in 20 mL of 1.0 mgL^{-1} mercury standard, stirred at 200rpm for 30minutes**.** Then, the solution was filtered and filtrate was analyzed by AAS via cold vapor method to check the unabsorbed concentration of Hg^{2+} ions. Initial and final concentration of samples was analyzed against mercury standard and results were obtained. Later on real samples were also collected from diverse drinking water sources and were analyzed before and after the adsorption.

Point of zero charge (pH_{PZC})

Point of zero charge tells the pH at which the net electric charge of cation and anion become zero on the adsorbent surface. The initial pH of solutions was adjusted by adding either NaOH or HCl in the range of 2-10. Then 20 mg of adsorbent were added in series of 50 mL conical flask containing 20 mL of pH adjusted solution and shaken for next 24 hours at ambient temperature at 200 rpm [20]. Afterwards, final pH values were noted and, the initial and final pH (pHf) values (pH=pHi - pHf) were plotted against the pHi. The point of intersection of the resulting curve pH_{PZC} value. The value of pH_{PZC} was found to be 5.1, which is shown in **Figure 4**. Above pH_{PZC} value adsorbent has negative charge. This result is in agreement with the obtained pH results at which optimum adsorption achieved.

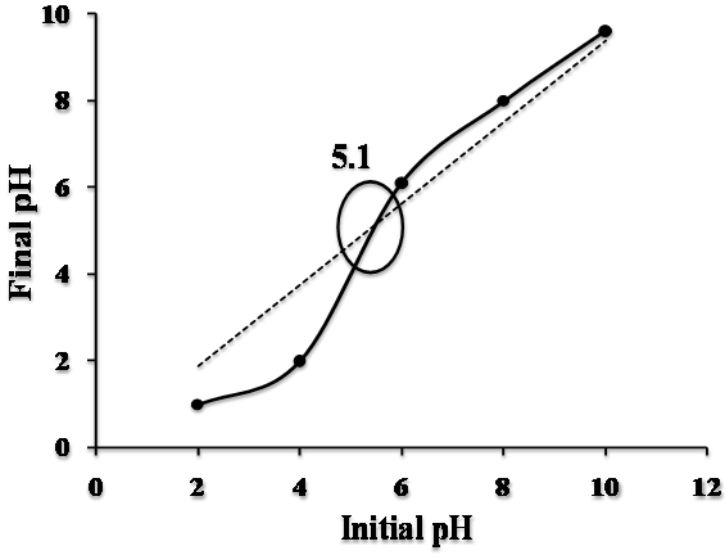

Figure 4. Plot of pHi vs. ΔpH to obtain point of zero charge (pHpzc) value for the IIP

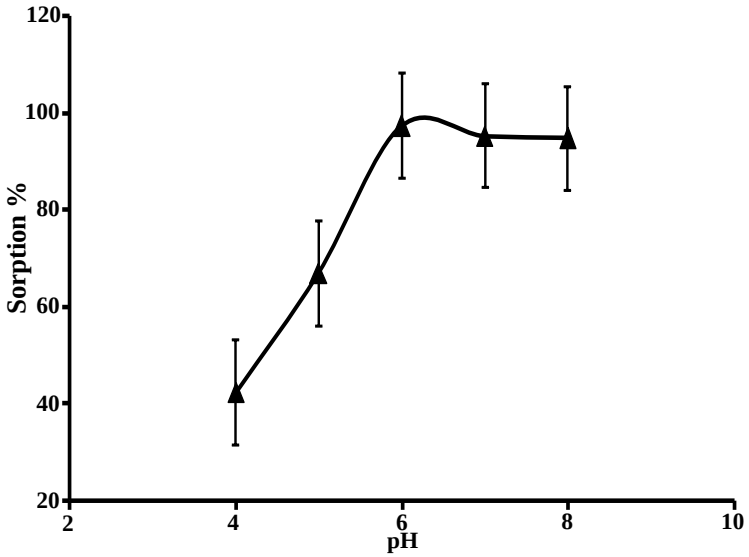

Figure 5. Effect of pH on adsorption of Hg^{2+} ions

Effect of pH

Adsorption of metal ion is firmly pH dependent, thus effect of pH studied by equilibrating 20 mg of polymer as adsorbent with 20 mL of aqueous solution containing 1.0 µg L^{-1} concentration of Hg^{2+} ions in adjusted pH range of 4-8. **Figure 5** shows the increased in extraction with the increased pH and maximum adsorption achieved at pH 6. Low extraction at decreased pH could be because of the hindrance of the H^{+}ion and as the mere pH increased protonation weekend and uptake of Hg^{2+} ions favored. Adsorption diminishes as the pH increases formation of OH^{-} ion increases. Therefore, pH of solution adjusted to pH 6 for the optimum extraction of Hg^{2+} ions [21].

Effect of contact time

The effect of sorption and desorption time on the adsorption of Hg^{2+} ions was also studied through a batch experiment as contact time plays vital role in the adsorption phenomenon. The adsorption of Hg^{2+} ions was investigated at 30 to 240 minutes at pH 6 and the results are presented in **Figure 6**. Initially the increase in adsorption was observed when reaction was proceeding from 30 to 60 and 90 minutes respectively. Maximum adsorption was accomplished in 90minutes. After the 90 minute reaction time the adsorption was declined which

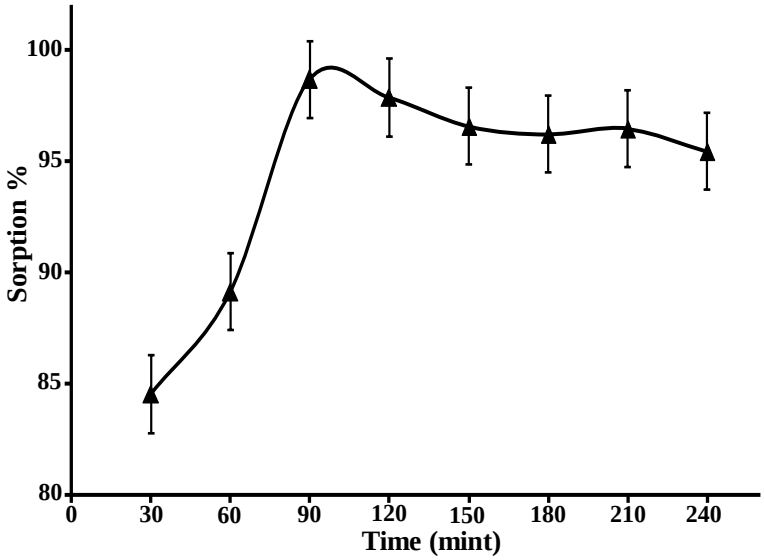

Figure 6. Effect of contact time on the adsorption of Hg^{2+} ions

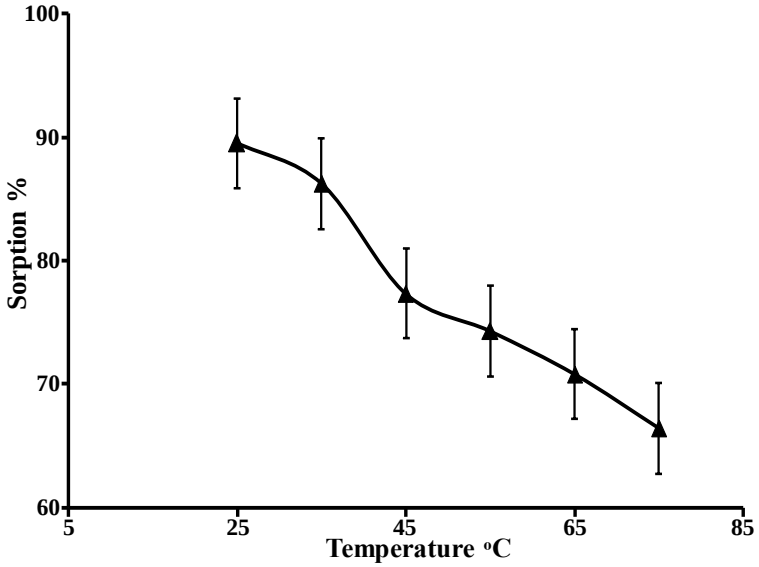

Figure 7. Effect of temperature on the adsorption of Hg^{2+} ions

could be due to disturbance of equilibrium established between sorbate and sorbent. Further reaction was conducted up to 240 minutes and checked the adsorption efficiency, and it was cleared from the data that with increase in time decrease in adsorption was observed. Therefore the 90 minute reaction time was taken as the optimum contact time for further studies [22].

Effect of temperature

Adsorption mechanism has great dependence on the temperature as the mobility of ions is greatly affected by the temperature and ions collide and attach with adsorbent when they easily move in solution. To investigate the temperature affect, adsorption studies were carried out at different temperatures from 25°C to 75°C at optimized pH and time and results are presented in **Figure 7**. At 25°C maximum adsorption of Hg^{2+}ions occurred and as the temperature increased a decline in adsorption of Hg^{2+} ions is observed from above it can be said that at high temperature adsorption is shifting toward desorption. So, 25°C were taken as the optimized temperature [23].

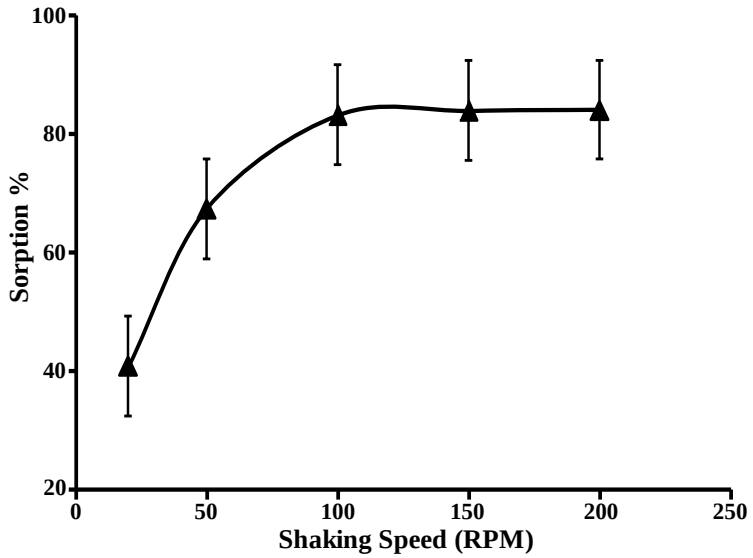

Figure 8. Effect of shaking speed on adsorption Hg^{+2} ions

Effect of shaking speed

Effect of shaking speed over the uptake of Hg^{2+}ions was also studied at different shaking speed from 20 to 200rpm via batch experiment with other optimum parameters. Initially rise in the adsorption was observed from 20 to 100rpm and optimum adsorption achieved at 100rpm, shown in **Figure 8**, while a little decline is noticed at increased shaking speed and it can be said at above shaking speed desorption occurred.

Adsorption isotherms

Adsorption isotherm for the sorption of Hg^{2+} ions was done at 25°C to check the efficiency of IIP. In present study Langmuir and Freundlich equation were tested.

$$\frac{1}{q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m}$$

where C_e (mg L^{-1}) is the amount of totalHg^{2+} ions in the solution, qe (mg g^{-1}) is the Hg^{2+} ions adsorption capacity at equilibrium. Q_m the monolayer adsorbent capacity and b is the energy Langmuirconstant of adsorption. The Q value was calculated from the slope of a linear plot of C_e/C_{ads} versus C_e. The correlated parameters were obtained by calculation from the values of the slope and intercept of the respective linear plot **Figure 9A**.

Freundlich is an empirical adsorption isotherm model which accounts for the multilayer adsorption by the adsorbent and favors the heterogeneous material. The linear Freundlich isotherm is given as:

$$\log C_{ads} = \log K_f + \frac{1}{n} \log C_e$$

where C_{ads} is the amount of mercury adsorbed per unit weight on the adsorbent (mg g^{-1}), whereas Ce is concentration of mercury in solution (mg L^{-1}) at equilibrium, K_f is the Freundlich capacity factor and 'n' is Freundlich intensity factor. Freundlich isotherm constants of the sorbent **Figure 9B**, were obtained from the slope and intercept calculation of the linear plot log C_{ads} vs. log Ce.

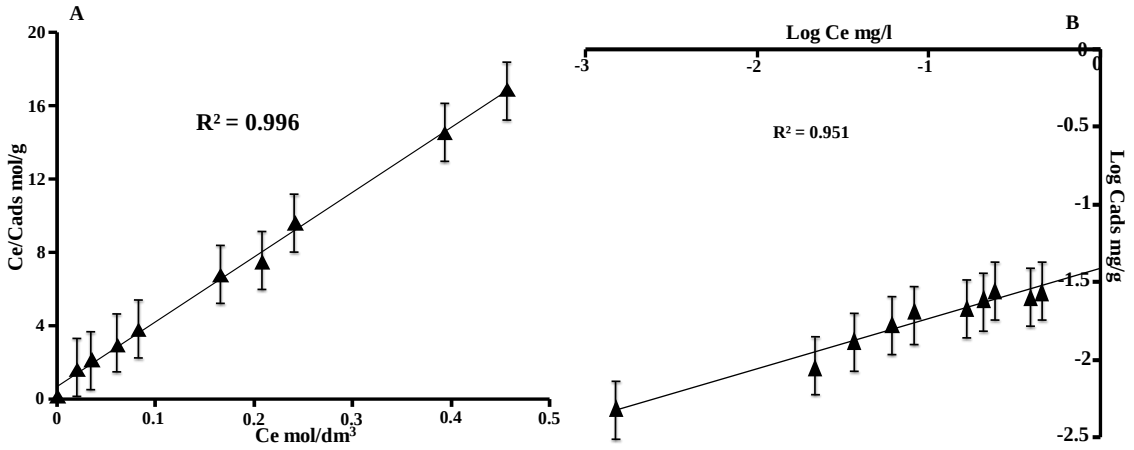

Figure 9. Langmuir adsorption isotherm (A) Freundlich adsorption isotherms (B)

Table 1. Mercury (II): Langmuir and Freundlich isotherm constants

Langmuir				Freundlich		
Q (mg/g^{-1})	L (L mg^{-1})	R_L	R^2	K_f (mg/g^{-1})	n	R^2
0.0282	51.96	0.018-0.161	0.996	0.346	3.11	0.951

The correlation coefficient (R^2) of Langmuir and Freundlich were calculated and presented in **Table 1** along with other results and, from it can be concluded that adsorption of Hg^{2+} ions by IIP best adjust in Langmuir equation and it's a monolayer adsorption.

Adsorption kinetics

In order to investigate the adsorption mechanism completely, adsorption equilibriums are needed to be equipped with adsorption kinetics [26] which helps in finding out the rate of metal ion adsorption and the time required to achieve equilibrium for mercury in aqueous environment. Pseudo first order and second order kinetic models were used to fix the experimental data. The pseudo first order rate constant K_1 was determined from the plot in **Figure 10A** in which log (qe -qt) versus t was plotted and a straight line was obtained for Hg^{2+} ion imprinted polymer and correlation factor value was (R^2=0.8907). The experimental data was further analyzed for pseudo second order kinetic model by plotting t/q against t in **Figure 10B** and the second order rate constant was determined from the plot with correlation factor (R^2=0.9994) and from above plots it can be concluded that pseudo second order kinetic model has good correlation for Hg^{2+} ions adsorption, and the Sorption kinetics constant obtained from the pseudo-first and second order models are given in **Table 2**. The Lagergren pseudo 1st order and pseudo 2nd order linearized models are given by equations (4) and (5).

$$\log(q_e - q_t) = \log q_e - k_{1ads}\frac{t}{2.303} \quad (4)$$

$$\frac{t}{q_1} = \frac{1}{k_2 q_e} + \frac{t}{q_1} \quad (5)$$

where:

- K_1,ads is Lagergren rate constant for first order sorption (min^{-1})
- K_2 is second order rate constant (g ug^{-1} min^{-1})
- qt is amount of adsorbate adsorbed at time t
- qe is amount of adsorbate adsorbed at equilibrium.

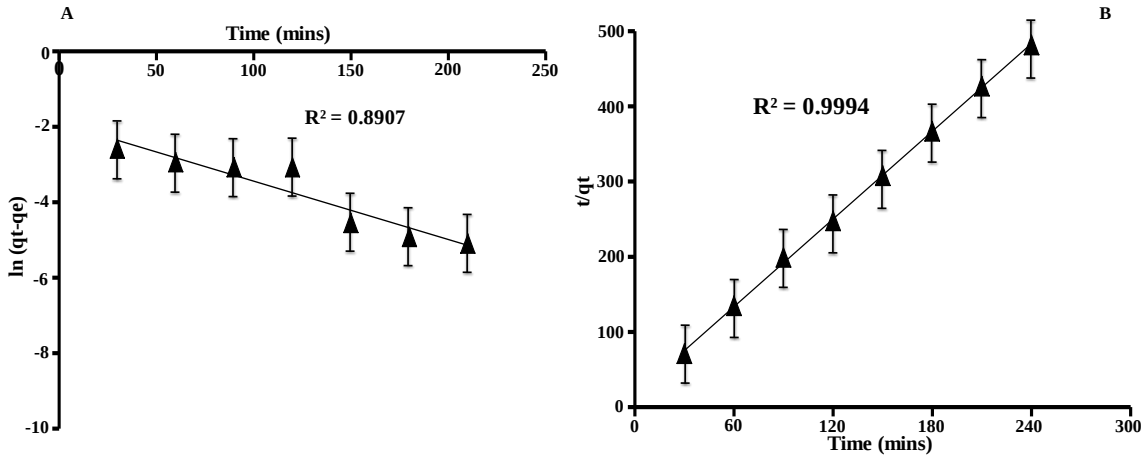

Figure 10. Pseudo 1st order kinetics (A) Pseudo 2nd order kinetics (B)

Table 2. Kinetic model parameters for the sorption of Hg^{2+} ions by IIP

Pseudo first order			Pseudo second order		
K_1 (min^{-1})	qe, cal (mg g^{-1})	R^2	K_2 (min^{-1})	qe, cal (mg g^{-1})	R^2
0.029	0.47	0.887	0.221	0.51	0.999

Table 3. K_d, K and k' values for Cu^{2+}, Cr^{3+}, and Co^{2+} with respect to Hg^{2+}

Metal ion	Non-imprinted polymer		Imprinted polymer		
	K_d	k	K_d	k	k'
Hg^{2+}	1.92		10.27		
Cu^{2+}	0.123	15.60	0.084	122	7.82
Cr3+	0.137	14.01	0.099	103	7.35
Co2+	0.311	6.17	0.013	76	12.31

Selectivity Study

The distribution and selectivity coefficient of competitive ions can be obtained by equilibrium data according to equation 1, 2 and 3. In equation 1 K_d is distribution coefficient, C_i and C_f are initial and final concentrations of metal ions. V is the volume of the solution in (mL) while m is the mass of adsorbent used in (g). k is the selectivity coefficient, X^{m+} represents competitiveions.

$$k_d = \left[\frac{(c_i - c_f)}{c_f}\right](v/m) \quad (1)$$

$$k = K_d(M^+)/K_d(X^{m+}) \quad (2)$$

A comparison of k values of imprinted polymer with non-imprinted polymer was given by relative selectivity coefficient k'

$$k' = k_{imprinted}/k_{non-imprinted} \quad (3)$$

Competitive adsorption of Hg^{2+} ions and other interfering ions which contain the same charge, nearly identical size and have good binding affinity with carboxylic group were also investigated via batch experiment. Cu^{2+}, Cr^{3+}, and Co^{2+} were chosen because they possess same atomic radii. Comparison of the K_d values for the IIP samples with NIP shows an increase in K_d for Hg^{2+} while K_d decrease for Cu^{2+}, Cr^{3+}, and Co^{2+}. The relative selectivity coefficient signifies the metal adsorption affinity of recognition sites for Hg^{2+} ions. **Table 3** shows that relative selectivity coefficient of imprinted polymer for Hg^{2+} / Cu^{2+}, Hg^{2+} / Cr^{3+} , Hg^{2+} /Co^{2+} were respectively 122, 103, 76 times greater than for non-imprinted polymer.

Analytical Application

Initially all procedures were performed in aqueous medium while optimization of parameters and later on, IIP was applied for decontamination of drinking water which were collected from diverse water sources available for drinking purpose in the region and, IIP showed efficient adsorption capacity for Hg^{2+} ions. Results show high amount of mercury contamination, it could be due to effluent discharged from industries without any treatment.

Table 4. Standard Addition to water sample method for Hg^{2+}n=5 (µg L^{-1} ± Error)

Sample	S1	S2	S3	S4	S5
Without addition	15.3**±0.6**	12.1**±0.5**	14.3**±0.71**	16.5**±0.51**	18.23**±0.62**
Hg^{2+}Added	5	5	5	5	5
Hg^{2+}Found	20.1**±0.7**	17.0**±0.61**	19.0**±0.55**	21.3**±0.39**	23.1**±0.45**
% recovery	96	98	94	96	97.4

Amount of mercury in all water samples were beyond permissible limit of WHO drinking water standards. The detoxification process of water samples was carried out at optimum conditions. The results are given in **Table 4**, which presents that mercury level in each sample decreased below acceptable limits.

CONCLUSION

In this paper an adsorbent Hg^{2+}ions imprinted polymer was synthesized via precipitation method in which bi functional reagent 1-vinylimidazole was used as a monomer and metal-complexing group and characterized successfully by FTIR, SEM and EDX. IIP showed higher selectivity for Hg^{2+}ions then other interfering ions Cu^{2+}, Cr^{3+}, and Co^{2+} based on selectivity study. Adsorption favors the second order kinetics and follows the Langmuir's isotherm. Fast and easy method for the synthesis of Hg^{2+} ions imprinted polymer is reported in this work. Focus of research work was detoxification of Hg^{2+} ions and IIP's are best alternative for removal of toxins from aqueous medium then earlier reported method.

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