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Chemistry

# INVESTIGATION ON PHYSICOCHEMICAL PROPERTIES OF NOVEL POLYMERIC COMPOSITES

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| **B. Rajeswari** | Research scholar & Post Graduate and Research Department of Chemistry Seethalakshmi Ramaswami College Tiruchirappalli-620 002. |
| **C. Dhivya** | Asst. Professor, Department of Chemistry, Jain University, Bangalore. |
| **R. Santhi*** | Associate professor, Post Graduate and Research Department of Chemistry Seethalakshmi Ramaswami College, Tiruchirappalli-620 002. *Corresponding Author |
| **N. Radha** | Associate professor (Retired), Post Graduate and Research Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620 002. |

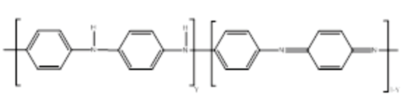
**ABSTRACT** Four new conducting polymers were synthesized by doping Polyaniline with Imidazole, Imidazolium chloride, Imidazolium dichloride and benzimidazole-Schiff base (2-(1H-indol-3yl)-N-(1-Phenylethylidine)ethanamine) by chemical oxidative polymerization of aniline using potassium persulphate as an oxidising agent. The polymer composites were characterized by UV-Visible and FT-IR spectroscopic techniques. In order to remove mercuric ions which are non-bio degradable, the adsorption characteristics of the Pani composites were studied through batch process. Sorption isotherms were constructed using Langmuir, Freundlich, Dubinin Radush-Kevich, Temkin and Redlich Peterson models. Thermodynamic parameters such as $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ were calculated to understand the spontaneity and randomness of the adsorption process. The morphology of the Pani composites before and after adsorption of HgCl2 on the surface of the Pani composites were found from PXRD, SEM and EDX spectra. The results of UV-Visible, FT-IR spectra, adsorption isotherms and morphological studies have revealed that the Pani composites are suitable adsorbents for the mercuric ions. The newly preared Pani composites are nano meter sized and are recyclable.

**KEYWORDS :** Nano Polyaniline composites, Adsorption of Mercuric chloride, recyclable

## INTRODUCTION

Environmental contamination by heavy metals is a widespread problem. Mercury and its salts cause environmental pollution due to the toxic effects on living beings. Mercury in its inorganic forms, attack mainly liver and kidneys in living beings. Discharge of Hg(II) ions cause severe environmental contamination as it is non-degradable and bio- accumulate in nature. Hence it is necessary to remove the Hg (II) ions from the environment[1-4]. There are several techniques such as ion exchange method, chemical precipitation, electrolysis, reverse osmosis, membrane filtration and adsorption to remove the heavy metal ions from the environment. Among the methods mentioned above, adsorption is an economical and efficient one because of its low cost, simplicity of designs and easiness of operation. Cross linked polymers and polymer composites have been used for the removal of Hg(II) ions from industrial waste water[5-8]. In the present work, polyaniline (Pani) and its composites from Imidazole and benzimidazole derivatives are used as adsorbents for the effective removal of Hg(II) ions from aqueous solutions. Polyaniline composites possess novel adsorption capacities as they are nano sized with large surface area compared to common adsorbents like silica gel and alumina.

Polyaniline is known to exist in different forms due to difference in the ratio of the imine-amine nitrogen. The value of Y in structure **1** varies from 0-1. Hence it is necessary to characterize the pani composites by UV-Visible and FT-IR spectral studies.



The derivatives of Imidazole used for preparing the composites can be easily blended with polyaniline. The four newly prepared polyaniline composites are used for adsorbing $HgCl_2$. The adsorption characteristics of pani composites are verified using Langmuir, Freundlich, Dubinin Radush-kevich, Tempkin and Redlich Peterson isotherms. The effect of varying the concentration of the adsorbate, time, temperature and pH. Optimization of the adsorption process is the main focus of the study. The reactivity and suitability of the four new pani composites are compared with PaniCl. The morphology of the pani composites before and after adsorption of $HgCl_2$ are found from PXRD, SEM and EDX studies.

## Experimental methods

## MATERIALS AND METHODS

All the chemicals and solvents used were of AR grade. Double distilled water was used for preparing the solutions. Mercuric chloride and potassium persulphate (AR, Sigma Aldrich) were used without further purification. Aniline (BDH) was distilled under reduced pressure before use. Other chemicals of AR grade were used as received. HCl and NaOH were used to adjust the pH of the solutions.

### Synthesis of Polyaniline chloride (PaniCl)

Aniline (2ml) was dissolved in 100ml of hydrochloric acid (1M). The mixture was stirred using a magnetic stirrer and 50ml of potassium persulphate (0.1M) was added dropwise to the aniline-acid mixture for about two hours with continuous stirring at room temperature. Stirring was continued for further 30 minutes to ensure complete polymerization. A dark green coloured PaniCl thus formed was filtered using a Whatmann No. 1 filter paper. The excess acid content and oligomers of aniline were removed by repeated washings with distilled water, ethanol, acetone and diethyl ether. The green coloured pristine polymer obtained was dried in an air oven for four hours till constant weight was reached.

The colour changes that appeared during the addition of potassium persulphate is given below.

Straw yellow →yellow→brown →green colour.

### Preparation of PaniCl-Im Composites

PaniCl (1g) and Im (1g) were mixed together and suspended in 15ml of alcohol and sonicated in an ultra sonic cleaning bath (NEY, 50 Khz) for 30 minutes. The slurry was centrifuged and the supernatant liquid was removed. Repeated washings with diethyl ether and sonication resulted in a free flowing dark coloured Pani-Im composite. In the case of PaniCl-ImCl and PaniCl-$ImCl_2$ , PaniCl (1g) was stirred with HCl (1ml & 2 ml, 0.1M) in the sonicator. Diethyl ether (15ml) was added and sonicated for 30 minutes. The resulting slurry was washed with ether and centrifuged. The resulting green coloured mass was dried in a vacuum desiccator to get a free flowing powder.

Preparation of Pani-benzimidazole Schiff base composite Pani-benzimidazole Schiff base composite preparation was carried out by an In-situ method. Aniline (0.01mmol) and Schiff base (0.01mmol) were mixed together in dilute acetic acid medium. Potassium persulphate (0.1M, 50ml) was added slowly during a period of 1 hour with continuous stirring at room temperature. The stirring was continued for another 30 minutes, after the complete addition of potassium persulphate. At the end of 60 minutes a green coloured pani composite resulted. The reaction product was filtered and washed with water. The dry greenish powder obtained was triturated with ethanol, acetone and ether to get a free flowing pani composite.

### Synthesis of benzimidazole Schiff base

Tryptamine (1.6g) was mixed with an equivalent amount of acetophenone in acetic acid, alcohol mixture at room temperature. The reaction mixture was refluxed for 6 hours. The solid product formed was filtered, washed with ethanol, dried over anhydrous $CaCl_2$ in a vacuum desiccator and recrystallised with alcohol.

### Spectral Characterizations

UV-Visible spectra of the pani composites were recorded in DMSO using Lambda 35 Perkin Elmer UV- Visible spectrophotometer (200-1100nm). FT-IR spectra of the samples as KBr pellets were measured using a Perkin Elmer FT-IR spectrometer in the range of 4000-400$cm^{-1}$. The Powder X-ray diffraction (PXRD) pattern of PaniCl - mercuric chloride after adsorption was recorded using Bruker D8 X-ray diffractometer, at a scan rate of 1 step/second. The powdered samples were irradiated with CuKα radiation and the analysis were performed from 20-80º (2Θ) with a step size of 0.001º. The SEM images of pani matrix before and after adsorption were recorded using Field Emission Scanning Electron Microscope (ZELSS).

### Sorption experiments- Batch process

Pani composites (2mg) were suspended in a solution of mercuric chloride (10 ml, 0.02M) and sonicated for 30 minutes at 30ºC. The slurry was centrifuged and 5ml of the supernatant liquid was pipetted out and titrated against KI solution by conductometric method. The concentration of mercuric chloride in the supernatant liquid was determined by plotting conductance Vs volume of KI required. The sorption curves were constructed from the concentration of mercuric chloride thus obtained after adsorption (Ce). The initial concentrations (Co) were in the range of 0.01-0.05M.

### Effect of temperature

Effect of temperature on the adsorption of $HgCl_2$ solutions on Pani Composites was studied at 5°C intervals ranging from 25°-40°C. Pani composites (2 mg) and $HgCl_2$ (10ml, 0.02M) were sonicated for 30 minutes, after which the concentration of mercuric chloride was determined.

### Effect of contact time

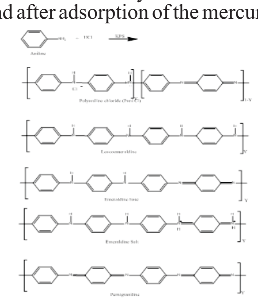
A known amount **(**2mg) of adsorbent was sonicated with 10ml of 0.02M of $HgCl_2$ solution at different equilibrium time (10-60minutes). The optimum time required for maximum adsorption of $HgCl_2$ was found to be 30 minutes.

### Effect of pH

The effect of pH on the adsorption capacity of Pani Composites was investigated in the pH range of 1-13. PaniCl-Im and benzimidazole composites (10mg) were suspended in 2.5ml of conductivity water. $HgCl_2$ (2.5ml, 0.05M) and different concentrations of hydrochloric acid (5ml, $10^{-1}$ to $10^{-6}$ M) were added and sonicated for 30 minutes. Similarly, NaOH solutions (5ml, $10^{-1}$ to $10^{-6}$M) were used for the alkaline pH.

## RESULTS AND DISCUSSION

Effluents from industries cause environmental pollution due to bioaccumulation of heavy metal ions in water and soil. Among the several heavy metal ions mercuric ions are difficult to remove from the water bodies. Hence it is necessary to remove mercuric ions[10] from the effluents. In the present work four new Pani composites are prepared from Pani Cl, Im, ImCl, $ImCl_2$ and benzimidazole- Schiff base. The free flowing nano sized adsorbent is used for adsorbing the Hg ions from aquous solutions . The PaniCl in the emeraldine salt form is prepared by chemical oxidative polymerization (Scheme 1). The Pani composites are characterized by UV-Visible and FT-IR spectral analysis before and after adsorption of the mercuric ions.



Scheme I Preparation of PaniCl and various oxidation states Polyaniline

### UV-Visible spectral analysis

The UV -Visible spectral data of Pani composites are listed in Table I. PaniCl and its composites exhibit two bands at 307-324nm and 580-621nm in DMSO solvent. The low nm band arises (Fig. 1a-d) due to the π-π* transition in the benzenoid rings of Pani. The longer wave length band is ascribed to the electron delocalization between benzinoid to quinoid rings. Hence it may be inferred that the polymer composites exist in the emeraldine form[11]. The pani composites after adsorption of $HgCl_2$ the UV-Visible spectra were recorded. The Pani composites exhibit a bathochromic shift for the benzenoid peak ~16-75nm (Table 1). The bathochromic shift implies that the adsorption of mercuric chloride enhances electron delocalization in the benzenoid ring. A hypsochromic shift of 2-18nm is observed for the quinoid ring in the pani composites from PaniCl and PaniCl-$ImCl_2$ implying that the electron delocalization in the exciton band is restricted. A bathochromic shift of 7-19nm observed for the composites of Im and ImCl and benzimidazole derivative implies that electron delocalization is favoured in the exciton band of the quinoid ring. Further, benzimidazole Schiff base derivative gives a highly intense exciton band probably due to the enhancement of inter molecular electron delocalization in several molecules of the composite.

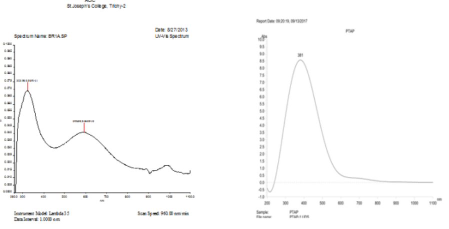


**Fig. 1a,b UV-visible spectra of PaniCl-Im and Pani–benzimidazole composites in DMSO.**

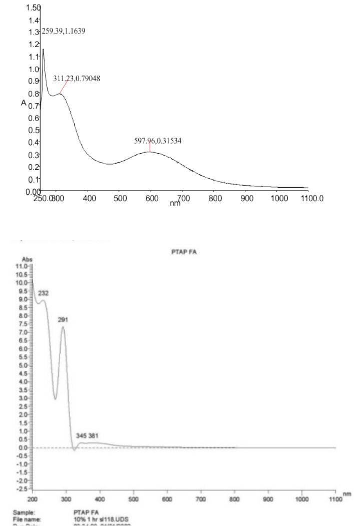



**Fig. 1a,b UV-visible spectra of PaniCl-Im- $HgCl_2$ and Pani –benzimidazole- $HgCl_2$ composites in DMSO**

### FT-IR spectra

FT-IR spectra of Pani composites showed a broad band in the region 3850-3000 $cm^{-1}$, which are assigned to the N-H, OH & CH stretching vibrations in the pani composites. The stretching frequencies at 1593-1579$cm^{-1}$ &1500-1413$cm^{-1}$ have been assigned to the C-C vibrations in the quinoid and benzenoid rings. The bands at 1378-1238 $cm^{-1}$ are assigned to the C-N stretching vibrations (Table II). The region of 1126-1039$cm^{-1}$ are due to aromatic C-H inplane bending modes. The C-H out of plane bending modes occur around 852-758$cm^{-1}$. For all Pani composites bands at 752-616$cm^{-1}$ are C-C bending vibrations and the band at 505-657 $cm^{-1}$ due to C-H in plane deformation modes. After adsorption of mercuric chloride , multiple absorption bands occur in the region of 3514-3000$cm^{-1}$. In all the pani composites $C{=}N^{+}H$ occurs at 2634-2365$cm^{-1}$. The bands have undergone a red shift of approximately 200 $cm^{-1}$ after adsorption of $HgCl_2$. The quinoid and benzenoid vibrations occuring at 1594-1562 & 1502-1483$cm^{-1}$ are red shifted after adsorption of $HgCl_2$. The red shift for C-N stretching vibration occuring in the region 1377-1244$cm^{-1}$ indicates strong interaction with the Pani skeleton due to the binding of $HgCl_2$ on the N atoms[11]. The strong vibrational band at 1125$cm^{-1}$ indicates that the electronic band resulting from the vibrational movement of functional groups are strongly affected by the binding of $HgCl_2$ to the N- atoms present in between the rings in the pani skeleton. Red shifts of increased intensity are observed for the bending vibrations (Table II) from 852-816,758-753,616-611 and 505-501$cm^{-1}$ .

**Adsorption studies of mercuric chloride on Pani composites**

The adsorption of mercuric ion by the Pani composites are studied by batch process. For all the adsorption process the reactant mixtures were equilibrated for 30 minutes. Concentrations of mercuric ions in the filtrate after the adsorption process are measured graphically by conductometric titration against KI solutions.

**Effect of variation of mercuric ion:**

In order to evaluate the adsorption capacity and the surface properties of adsorbent related to adsorption[11,13-18], it is essential to analyze the adsorption isotherms. In the present study Langmuir, Freundlich, Tempkin, Dubinin Radush- Kevich and Redlich- Peterson models are employed for the adsorption studies.

Langmuir model

The Langmuir model[9] in the form of the linearised equation (1) is used to calculate the maximum amount of $Hg^{2+}$ ions adsorbed ($q_m$) by Pani and its composites. From the plot of $1/q_e$ vs $1/C_e$ , it can be observed that the adsorption obeys the Langmuir model. The Langmuir constants $q_m$ and $K_L$ determined from the slope and intercept of the plot are presented in Table III.

$1/q_e = 1/ K_L q_m C_e + 1 / q_m$ …………………(1)

In Langmuir equation(1) $q_m$ is the maximum monolayer adsorption capacity of the adsorbent (mg/g).

It can be observed from Table III that the $q_m$ value is the highest (0.61mg/g) for Pani-Im composite with $K_L$ (3.1719 L/g) and hence the Langmuir model is best fitted for Pani-Im composite.

**Freundlich isotherm**

The Freundlich adsorption isotherm describing the sorption equilibrium for both monolayer and multilayer adsorption[9,18] is represented by equation (2),

$\log q_e = \log k_F + 1/n \log C_e$…………………(2)

where $k_F$ denotes adsorption capacity and n is related to the intensity of adsorption. From the plot of log $q_e$ Vs log $C_e$ the Freundlich isotherm constant $k_F$ (sorption capacity) and 1/n (intensity of sorption) are calculated and the corresponding correlation coefficient $R^2$ are shown in Table III. The highest value of 2.598 is found for PaniCl-Im$Cl_2$ & Pani benzimidazole composites suggesting multilayered formation is favoured for the two composites.

**Dubinin Radush-kevich isotherm**

Dubinin Radush-kevich (DR) isotherm has been usually applied to distinguish the physical and chemical adsorption of metal ion.

The Linear form of DR isotherm is

$\ln q_e = \ln q_D - B\varepsilon^2$…………………. (3)

A plot of lnqe Vs $\varepsilon^2$ gives a linear trace and the constants $q_D$ & B calculated from the slope and intercept are shown in Table III. The isotherm constant B is the highest for PaniCl-ImCl (4.951). This model meant for estimating the physical nature of adsorption is found to be suitable for PaniCl - ImCl.

**Temkin isotherm**

Temkin isotherm is used to study the adsorbent –adsorbate interactions[9]. This model assumes that heat of adsorption of all molecules in the adsorbent layer would decrease with coverage of surface with adsorbent.

The linear form of Temkin isotherm is represented by equation (4)

$q_e = B_T \ln A_T + B_T \ln C_e$ ………………………..(4)

The Temkin isotherm equilibrium binding constant ($A_T$) and the Temkin heat of adsorption ($B_T$) are calculated from the slope and intercept of the plot $q_e$ Vs ln$C_e$. The Temkin heat of adsorption $B_T$ is found to be high for PaniCl-Im. The greatest binding energy and binding constants are observed for PaniCl-Im composite.

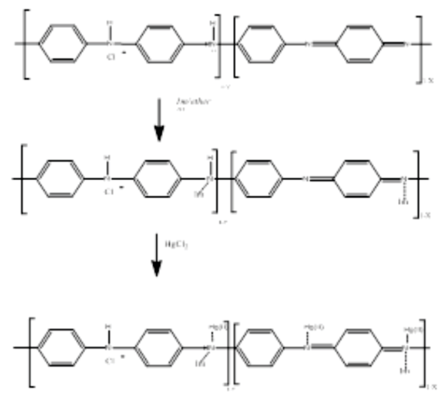
Redlich-Peterson isotherm

Redlich-Peterson isotherm represents adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility. The mathematical form of this isotherm is given by equation(5).

$C_e/q_e = 1/K_{RP} + \alpha_{RP}/K_{RP} Ce^{\beta}$ ………………. (5)

Where, $K_{RP}$, $\alpha_{RP}$ and β are constants. A plot of Ce/qe Vs Ce is linear and the constants $K_{RP}$, $\alpha_{RP}$ calculated from the slope and intercept are shown in Table III . The highest $K_{RP}$ value of 27.77 is found for PaniCl-Im$Cl_2$ ($R^2$= 0.965) indicating heterogeneous adsorption. The lowest $K_{RP}$ value of 0.769 is favoured for Pani-benzimidazole composite suggesting homogeneous adsorption.

Among the four composites studied PaniCl-Im is best fitted for Langumuir and Temkin model, It is observed that monolayer adsorption and adsorbent-adsorbate interactions are favoured for PaniCl-Im composite. PaniCl-Im$Cl_2$ and Pani benzimidazole composites exhibit the best fit for Freundlich model and Redlich Peterson model implies the multilayer adsorption. From the analysis of Redlich Peterson model the PaniCl- Im$Cl_2$ composite indicate heterogeneous system and Pani benzimidazole indicate homogeneous system. The Dubinin RadushKevich isotherm model is favoured for PaniCl-ImCl composite.



**Scheme II. Mechanism of Hg(II) removal by Pani-Im composites**

Effect of variation of Temperature

Inorder to verify the influence of temperature[19-22] on the adsorption process , the adsorption of mercuric ions by the pani composites are examined in the range of 298-313 K. The distribution coefficients (Kd) are calculated using the equation (6).

$K_d$ = qe/Ce……………………. (6)

Where qe is the amount of metal adsorbed on the unitary sorbent mass at equilibrium and Ce equilibrium concentration of metal ions in solution.

The standard free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) are calculated from Van't Hoff equation (7)

$\Delta G^0 = -RT \ln K_d$ ……………………… (7)

Where R= universal gas constant (8.314 J $mol^{-1}K^{-1}$)

The slope and intercept of the Von't Hoff plot of lnKd Vs 1/T are used to determine the values of $\Delta H^0$ and $\Delta S^0$.

$\ln K_d = -\Delta H^0/RT + \Delta S^0/R$ ………………….. (8)

Thermodynamic parameters such as standard free energy of adsorption ($\Delta G^0$), standard enthalpy of adsorption ($\Delta H^0$) and the standard entropy of adsorption ($\Delta S^0$) are very helpful for understanding the adsorbent-adsorbate system. The negative value of $\Delta G^0$ indicates the feasibility of adsorption (Table IV). The exothermic nature of adsorption is found from $\Delta H^0$ values. The positive value of $\Delta S^0$ for all the pani composites shows the spontaneity of the adsorption proceeds.

**Sorption - desorption study**

Sorption-Desorption of $Hg^{2+}$ ions by Pani[12] is mostly reversible and the processes can be controlled by changing the pH of the solution. The pH of the solutions are varied from 1-13 by using different concentrations of HCl and NaOH. In the acidic range pani exists as pani (+) and mercuric chloride is adsorbed on to the active sites through chloride bridge and H-bonding. In the alkaline range 9-13 pani exist in EB form and the adsorbed $HgCl_2$ is desorbed. The desorption ratio of Hg(II) using 0.1M HCl and 0.1M NaOH are calculated for Pani-Im and Pani benzimidazole composites (Table V). The desorption ratio is found to be 66% and 62.7% for PaniCl-Im and Pani benzimidazole composites respectively. It has been observed by earlier workers that 61.7% of the Hg ion is adsorbed on Pani Humic acid composite and desorbed by a solution containing 0.1M HCl and 0.5% thiourea solution[11]. The advantage of the present work is the adsorbed mercuric ions on the Pani composites are higher than that reported by earlier workers. The presence of Im and benzimidazole on the pani backbone matrix may be the reason for the higher adsorption/ desorption ratio.

### XRD

The XRD patterns for PaniCl-Im and PaniCl-benzimidazole are shown in Figures 2a & b. For PaniCl-Im $HgCl_2$ composite several sharp peaks (Fig. 2a) in the region of 10˚-60˚(2Θ) with a step size of $0.001^0$ is observed. The average particle size (D) is calculated from Debye Scherrer's formula (9).

$D = 0.9/\beta \cos\theta$ ………………..(9)

Where = wavelength of CuK radiation (1.54Å), β= full width at half maximum of peaks. The Partice size varies from 40-160 nm for PaniCl-Im-$HgCl_2$ composite. In Fig 4b the XRD pattern of PaniCl-benzimidazole- $HgCl_2$ has a broad amorphous scattering peak at about 2Θ= 21.5 and $27.5^0$ which are the characteristic peak of Pani. the particle size calculated using Debye Scherer's equation (9) is found to be 7&9nm. The adsorbed $HgCl_2$ can cause agglomeration of several crystallides[11] resulting in loosely entangled agglomerates. The results of the adsorption studies of PaniCl-Im-$HgCl_2$ indicate monolayer formation and that adsorbent-adsorbate interactions are well defined. The results of the adsorption studies for Pani-benzimidazole-$HgCl_2$ show multilayer adsorption.

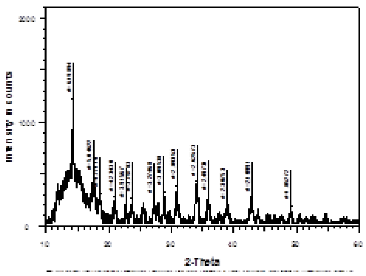



**Fig. 2a Powder XRD spectral analysis of mercuric chloride on PaniCl-Im**

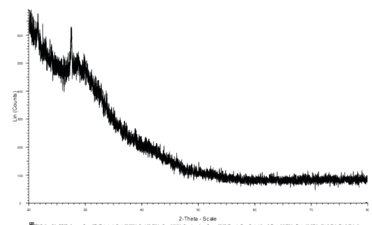
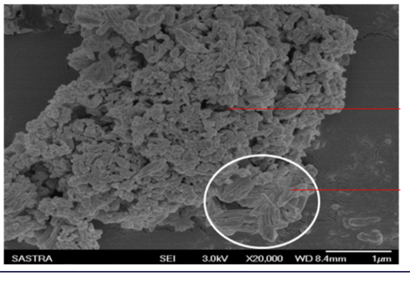



**Fig.2b. Powder XRD spectral analysis of mercuric chloride on Pani-benzimidazole**

### SEM

The SEM picture of PaniCl-Im and PaniCl-benzimidazole before and after adsorption of $HgCl_2$ is showed in Fig. 3a-d. The sem pictures before adsorption are of small spherical morphology. After adsorption the particles are larger, rod shaped and non-uniform in their size distribution[23]. The embedded molecules of $HgCl_2$ on Pani backbone are clearly visible.



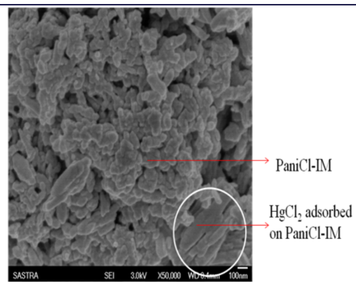




**Fig.3 a, b SEM analysis of before and after adsorption of HgCl2 on PaniCl-Im**

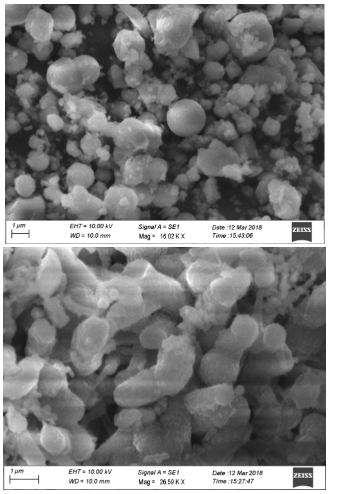


**Fig.3 c,d SEM analysis of before and after adsorption of HgCl2 on PaniCl-benzimidazole composite**

### EDX

The presence of a highly intense and broad peak in the EDX spectrum of PaniCl-Im composite (Fig. 4) at scan time 2.2-2.5 indicates the presence of $HgCl_2$ on pani backbone along with chloride peak at 0.5. Further four low intense peaks are found at the scan time of 8-12. These peaks may be due to the presence of Hg in different oxidation states (Hg(II), Hg(I), Hg(0), Hg). Pani being a conducting polymer exist in different oxidation states and can switch electrons between the variable oxidation states. The adsorbed mercuric chloride can interact with the pani backbone through inter and inra molecular electron transfer resulting in good adsorbent-adsorbate interactions.

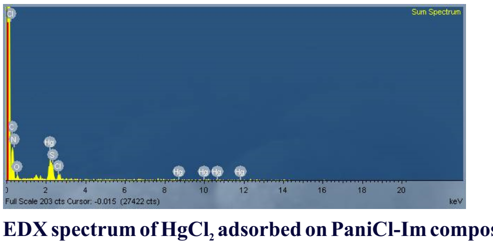



**Fig.4c EDX spectrum of $HgCl_2$ adsorbed on PaniCl-Im composite**

### CONCLUSION:

Four new pani composites from imidazole, imidazolium chloride salts and benzimidazole schiff base are synthesized by chemical oxidative polymerization. The newly synthesized polymers are characterized by UV-Visible and FT-IR spectroscopic techniques. Sorption capacity of pani composites are evaluated by analyzing five isotherm models. PaniCl-Im is best fitted for Langumuir and Temkin models, It is observed that monolayer adsorption and adsorbent-adsorbate interactions are favoured for PaniCl-Im composite. PaniCl-Im$Cl_2$ and Pani benzimidazole composites exhibit the best fit for Freundlich model and Redlich Peterson model implying multilayer adsorption. The Dubinin Radush-Kevich isotherm model is favoured for PaniCl-ImCl composite. The thermodynamic parameters $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ indicate that the adsorbent-adsorbate interactions on Panicomposites by $HgCl_2$ are favoured.

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