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Selective Adsorption and Detection of Heavy Metals from Aqueous Media using An Efficient Schiff-Base Resin (Polymethylene-bis(2-methoxy-1-napthaldehyde),m- xylenediimine

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"Selective Adsorption and Detection of Heavy Metals from Aqueous Media using An Efficient Schiff-Base Resin (Polymethylene-*bis*(2-methoxy-1-napthaldehyde),m-xylenediimine

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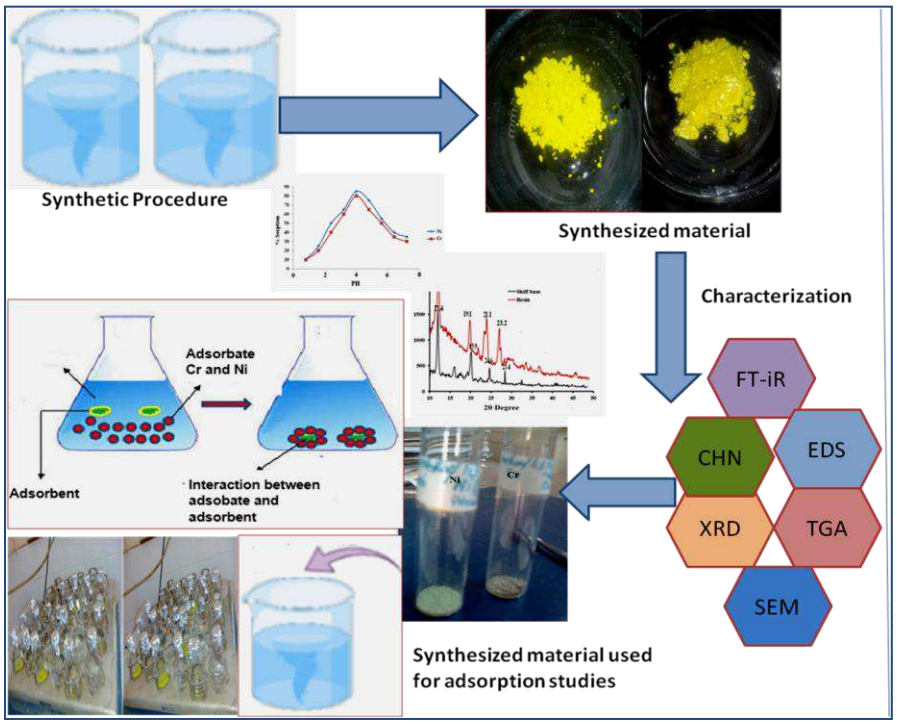
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ABSTRACT

The Present study examine the synthesis of a novel compounds Schiff base *bis*(2-methoxy-1-napthaldehyde) m-xylenediimine, and Schiff based resin Polymethylene*bis*(2-methoxy-1-napthaldehyde),m-xylenediimine (PMBMNMXD).After the preparation of synthesized material were identified and characterized by different instrumental techniques for evaluate structure and surface morphology. The synthesized compounds were characterized *via* different spectroscopic techniques; (CHN), (FT-IR),(TGA),(EDS), (SEM), and (XRD) analysis. The synthesized resin has high adsorption capacity, stability and high efficiency, especially for metal ions. The synthesized material was used for uptake studies with Ni(II) and Cr(VI) ions. The optimum conditions were calculating by different parameters used to describe the effects of uptake including initial concentration, temperature, time, and pH through batch adsorption methods Schiff based resin will be used in adsorbents for removal of toxic metals from aqueous solution and wastewater treatment. The kinetic studies isothermal, thermodynamic and stability parameters will be studied and application of the proposed method on environmental water samples. The sorption results were used to examine different sorption isotherms like, Langmuir, Freundlich and kinetic studies such as, pseudo first order kinetics and pseudo second order kinetics. The *slope* and *linear plot* was used to evaluate the sorption isotherms. The polymeric resin PMBMNMXD was used for removal of Cr (VI) and Ni(II) ions in real water samples from different agricultural cities of Sindh (Province of Pakistan) such as Sanghar, Nawabshah, Kotri, and Jamshoro. The synthesized resin, PMBMNMXD were beneficial for industry because of their extraordinary adsorption properties for specific metal ions.

Key words. Isotherms, First order kinetics, , Spectroscopy,. CHN analysis, Thermodynamic

Graphical Abstract



1. Introduction

Schiff base resins are generally insoluble materials and exhibit poor solubility in most organic solvents, along with sharp melting points **[1-2]**.. Schiff base resins have consistently attracted the interest of researchers because of their wide range of applications in various fields of industrial and biological sciences **[3-4]**. Chelating resins can be readily regenerated after binding with metal ions **[5]**..Schiff base resins constitute an important class of ligands that have been extensively studied in coordination chemistry due to their unique electronic and catalytic properties **[6]**. Epoxy resins are characterized by the presence of an epoxide group before curing and may also contain aliphatic, aromatic, or heterocyclic structures, as well as metal complexes **[7].** The structure of a Schiff base chelating resin has a direct influence on its suitability for the pre-concentration and separation of metal ions**[8]**.The Schiff base chelating resin was found to be effective in the removal of heavy metal ions from real wastewater samples. The effects of various parameters, including initial metal ion concentration, contact time, temperature, and pH, on the adsorption of Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, and Co^{2+} ions were investigated. The adsorption

capacity of the resin for the studied metal ions was found to range from 29.95 to 157.25 mg g^{-1} **[9-10]**.

An adsorbate is a substance, such as atoms, molecules, or ions, present in a liquid or gaseous phase that is adsorbed onto the surface of an adsorbent. In general, the equilibrium uptake of an adsorbate increases with an increase in its concentration in the solution.

$$X/m=kP^{1/m}.$$

X=quantity adsorbed, m= mass of adsorbent, *P* is the pressure of adsorbate and K and n are empirical constant **[11-12].**.The Langmuir adsorption model quantitatively describes the formation of a monolayer of adsorbate molecules on the homogeneous surface of an adsorbent as a function of the adsorbate concentration in the liquid phase with which it is in contact **[13]**. Several factors influence the adsorption process, including the pore structure and surface area of the adsorbent, the pH of the solution, the nature of the adsorbate, and the contact (agitation) time between the adsorbate and the adsorbent **[14]**. The removal of heavy metal ions from wastewater and contaminated soil is of great importance because of their toxic effects on human health and the environment. Various techniques, including adsorption, ion exchange, dialysis, precipitation, and solvent extraction, have been widely employed for the treatment of wastewater containing excessive concentrations of heavy metal ions **[15]**. .The presence of heavy metals in the environment has become a major concern due to their high toxicity to humans and ecosystems, even at low concentrations. Lead (Pb) is one of the most common and hazardous heavy metals because of its persistence and severe toxic effects. In addition, many industries, including the textile, paper, tissue, and plastics industries, use synthetic dyes to color their products and discharge large volumes of dye-containing wastewater into the environment. Among the available treatment methods, adsorption using low-cost adsorbents is considered one of the most effective and economical techniques for the removal of dyes. Consequently, a wide variety of non-conventional adsorbent materials have been investigated for this purpose **[16-17]**. Metal ions are non-biodegradable and, therefore, persist in the environment. Their accumulation above permissible levels can cause serious toxic effects. Copper is an essential trace element for many biological systems; however, excessive exposure to copper can be toxic **[18]**.

Heavy metal ions are among the most hazardous environmental pollutants because of their toxicity and tendency to bioaccumulate in living organisms. Since the human body cannot effectively metabolize or eliminate these metals, their accumulation may lead to various diseases and physiological disorders **[19]**. Schiff bases containing multidentate coordination sites readily form stable complexes with transition metal ions. When incorporated into a polymer matrix, Schiff base ligands exhibit high affinity and selectivity toward transition metal ions, making them promising materials for metal ion separation and recovery **[20]**. Chelating resins can be readily regenerated after metal ion adsorption and offer significant advantages over activated carbon and conventional ion-exchange resins due to their high selectivity and excellent sorption performance in metal ion removal processes **[21].**. The mechanism of corrosion protection of these materials was showing to adsorption of these materials on metal surface. It was described that the adsorption can be determined by not only by the nature and charge of the metal but also on the chemical structure of the inhibitor **[22]**. The metal ion uptake studies was accomplished studies by both batch and column techniques. In the batch technique, a suspension of the resin on the metal solution of known volume and concentration was agitated for a fixed time period over hot plate/ magnetic stirrer **[23]**. The adsorption of metal ions using chelating resins is widely preferred because of their low cost, high adsorption capacity, excellent chemical and thermal stability, and high removal efficiency, particularly for metal ions present at low or moderate concentrations. Consequently, chelating resins have been extensively employed for the removal of metal ions from aqueous solutions and in wastewater treatment applications **[24]**. The development of high-performance chelating resins for the removal of heavy metal ions from aqueous solutions has become an important research priority in environmental science. In addition, these materials have attracted considerable interest in the fields of inorganic catalysis and the recovery of valuable trace metal ions **[25]**. Magnetic chelating resins have also been developed for the removal of heavy metals from aqueous solutions. These resins can be easily separated from aqueous media using an external magnetic field and generally exhibit higher adsorption capacities than conventional non-magnetic resins **[26]**. Chelating polymer resins have gained significant attention as selective adsorbents for metal ions in wastewater treatment because of their high thermal and chemical stability, excellent selectivity, and ease of regeneration **[27-28]**. Adsorption is a surface phenomenon in which atoms, molecules, or ions accumulate on the surface of an adsorbent, whereas the removal of the

adsorbed species from the surface is known as desorption **[29].** Several treatment methods, including adsorption, ion exchange, dialysis, and solvent extraction, are commonly employed for the purification of water contaminated with heavy metal ions **[30]**. A wide variety of non-conventional adsorbent materials have also been investigated for this purpose **[31-32.]**The adsorption process is influenced by the type of metal ion and the chemical structure of the binding sites present on the adsorbent **[33]**. The human body cannot metabolize heavy metals and exhibit bioaccumulation properties resulting in many diseases and disorders **[34]**. The Langmuir adsorbent model describe the arrangement of only one layer of molecules on the surface of the adsorbent **[35]**. Batch methods using resins and solutions include well definite concentrations and volumes can be used to calculate adsorption **[36]**. The Schiff based resin structure consist of functional groups like azomethine, OH, and damine, the donor N and O atoms which can coordinate cationic metal ions, supported by the active adsorption of chromium(VI) and nickel(II). In this study, the synthesized resin PMBMNMXD was used for uptake studies with Cr(VI) and Ni(II) ions. Optimum conditions were established by exploring the effects of initial adsorbate concentration, contact time, temperature, and pH on adsorption performance via batch adsorption evaluation and Langmuir and Freundlich isotherm models. The purpose of this work is also to observe that resin PMBMNMXD successfully removed both ions from water samples. The polymeric resin PMBMNMXD was used for removal of Cr (VI) and Ni(II) ions in real water samples from different agricultural cities of Sindh (Province of Pakistan) such as Sanghar, Nawabshah, Kotri, and Jamshoro. The synthesized Schiff based resins are the beneficial for industry because of their extraordinary adsorption properties for specific metal ions **[37]**.

2. Experimental

2.1. Reagents and instrumentation

All starting materials and reagents, acetic acid, formaldehyde, diethyl ether, methanol, ethyl acetate, *n*-hexane, and NaOH were obtained from E. Merck, Germany. 2-methoxy-1-napthaldehy, m-xylenediamine were purchased from Alfa Aesar, Germany Deionized water was used during adsorption studies.1,5-Diphenyl carbazide (CAcom-plexion agent) was used for the preparation of sorbent. Thin-layer chromatography was carried out on pre-coated silica gel aluminum plates (Kieselgel,60, 254, E. Merck, Germany).Visualization of TLC chromatograms was performed at wavelengths of 254nm and 365 nm.SEM analysis were recorded on model JSM-6380 lv.XRD analysis were recorded D8-Bruker.FT-IR spectra were recorded on Thermo Nicolet Corporation,SF-AV 400 USA.

2.2. Methodology

2.2.1. General procedure of synthesis of Schiff base (BMNMXD)

2-methoxy-1-napthaldehyde (0.345g, 2mmol) was dissolved in ethanol,few drops of glacial acetic acid were added in the reaction mixture, m-xylenediamine (0.03ml, 1mmol) was then added and reaction mixture was then kept on refluxing for 2-3 hours. The progression of the reaction was monitored through TLC. The recovered yellow precipitate was filtered and washed with n-hexane and dried in an oven for 4-5 hour at the temperature 70°C -80°C to get pure product [38].The products was recrystallized from rethanol. The reaction scheme of BMNMXD is shown in **Figure 1.**

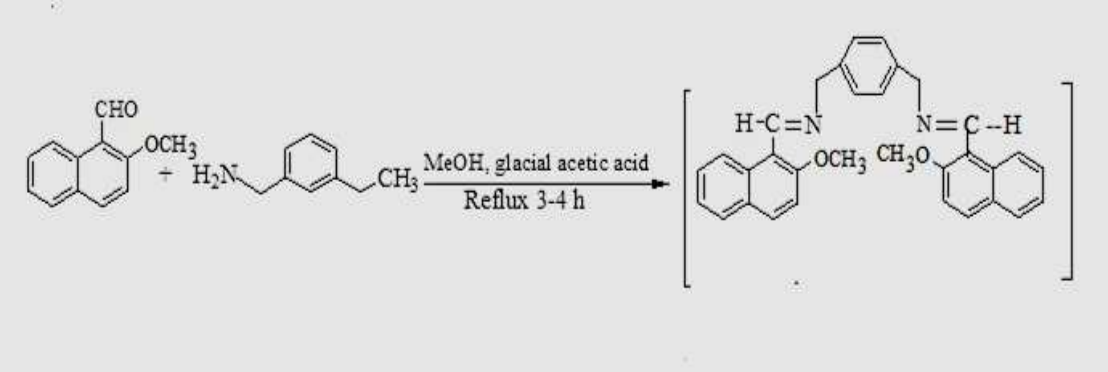


Figure 1. Reaction scheme to form Schiff base BMNMXD.

2.2.2. General procedure of synthesis of Schiff base resin (PMBMNMXD)

An amount of 1 g of was dissolved in 25 mL distilled water. The solution was kept on stirring for 10 to 15 minutes. 15 drops of 2M NaOH was then added and the reaction mixture was heated, refluxed to 60˚C for 5 minutes, pure solution of 37% HCHO was then added (1:3 molar ratio).The reaction mixture was further refluxed in oil bath at 120˚C for 2 hour. The recovered was filtered washed with water and diethyl ether and dried for 1-2 h at 80 ˚C.The reaction scheme of PMBMNXD is shown in Figure 2.

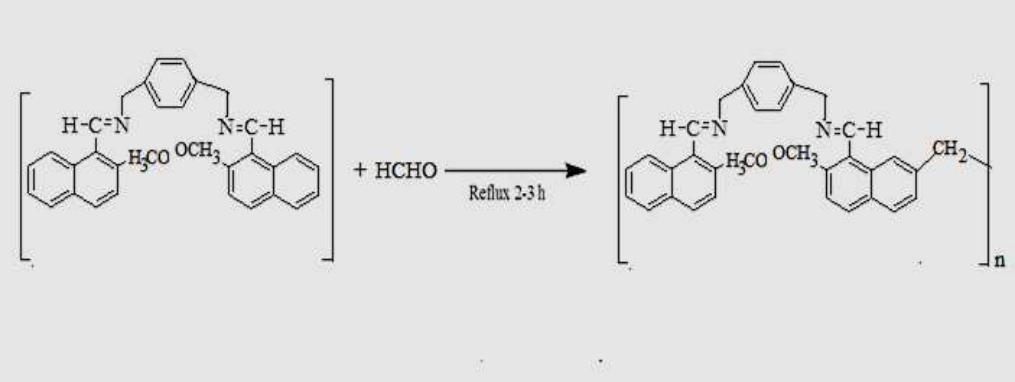


Figure 2. Reaction scheme of Schiff base resin PMBMNMXD



Figure 3. Synthesized Polymeric Resin

2.2.3. Adsorption study

Schiff based resin served as an absorbent for many metal such as Cu^{+2} ,Ni^{+2} ,Cr^{+2},Zn^{+2},Cd^{+2} etc. Because it's amino group $–NH_2$ can serve coordination site. It has much use feature including hydrophilicity, biocompatibility, biodedability and antibacterial antimicrobial activities. For removal of heavy metals, adsorption is considered as one of the most popular technique compared to other methods due to its low cost, abundant availability, simple process design with high removal efficiency, easy mode of operation and biodegradability.

2.2.4. Adsorption study by batch methods

The adsorption of Cr (VI) and Ni(II) from aqueous solution was studied at various temperatures using batch mode experiments. The adsorption of Cr (VI) and Ni(II) was totally dependent on parameters such as pH, concentration of the solution, effect of time, effect of Temperature and effect of does study.

2.2.5. Analytical method

An amount of 100 mg of 100 mesh size of resin (PMBMNMXD) was added in a aqueous solutions (10µg/ml) of Cr(VI) and Ni (II). A buffer was used to control pH.. A resin suspension on the metal solution of well-known concentration and volume (10 ml) were processed with 100 rpm for a fixed time period with the help of a thermostatic shaker. The thermostat shaker used for metal up takes study by batch method shown in Figure 4.The "*polymeric complex"* was filtered and washed with deionized water. The *recovered filterate* along with *washings* was investigated, by using UV-visible spectroscopy. The results obtained were used to calculate the percentage of metal ion uptake by the complexes and the distribution coefficient (K_d) values were calculated **[39]**.



Figure 4. Thermostat shaker used for metal up takes study by batch method

2.2.6. Data manipulation

The investigated data was helpful in calculating the percentage of metal ion loading and the distribution coefficient (kd), by using the equation:

$$\%\ Adsorption = \frac{C_i - C_f}{C_i} \times 100$$

$$K_d = \frac{Amount\ of\ analyte\ in\ adorbent}{Amount\ of\ analyte\ in\ solution\ at\ equilibrium} \times \frac{Volume\ of\ solution(ml)}{Mass\ of\ adsorbent(g)}$$

Where **Ci**, initial concentration and **Cf** final concentration of metal ions in solution. "***K_d***" is the distribution coefficient.

3. Results and discussion

3.1. CHN elemental microanalysis

The CHN elemental microanalysis table showed that all the results of C.H.N elemental microanalysis of Schiff bases and Schiff based BMNMXD resin PMBMNMXD approved with the calculated values , confirmed that the formation of proposed compounds.

CHN elemental microanalysis results are shown in **Table 1**.

Table.1 CHN analysis of BMNMXD and PMBMNMXD

			Calculated % (Found)		
Compounds	Chemical Formula	Melting Point	C	H	N
BMNMXD	$C_{23}H_{25}N_2O$	92 °C	74.11 (75.20)	6.65 (6.55)	5.89(6.77)
PMBMNMXD	$C_{23}H_{27}N_2O$	98 °C	75.41 (76.56)	7.76 (6.35)	6.74 (7.14)

3.2. FT-IR analysis

The spectra of Schiff base BMNMXD clearly determine>C=N azomethine peak at about 1670 cm^{-1}, a medium intensity peak. The FT-IR spectra of resin PMBMNMXD showed that the strong band at1671 cm^{-1}.The 1 cm Shift of band position in resin toward higher frequency confirmed the formation of resin as it differentiated a Schiff base from resin, the higher wave number and high intensities absorption bands due to poly condensation confirmed the formation of resin PMBMNMXD **[40].**.FT-IR spectra of BMNMXD and PMBMNMXD are shown in **Figure 5 (a) and Figure 5 (b).**

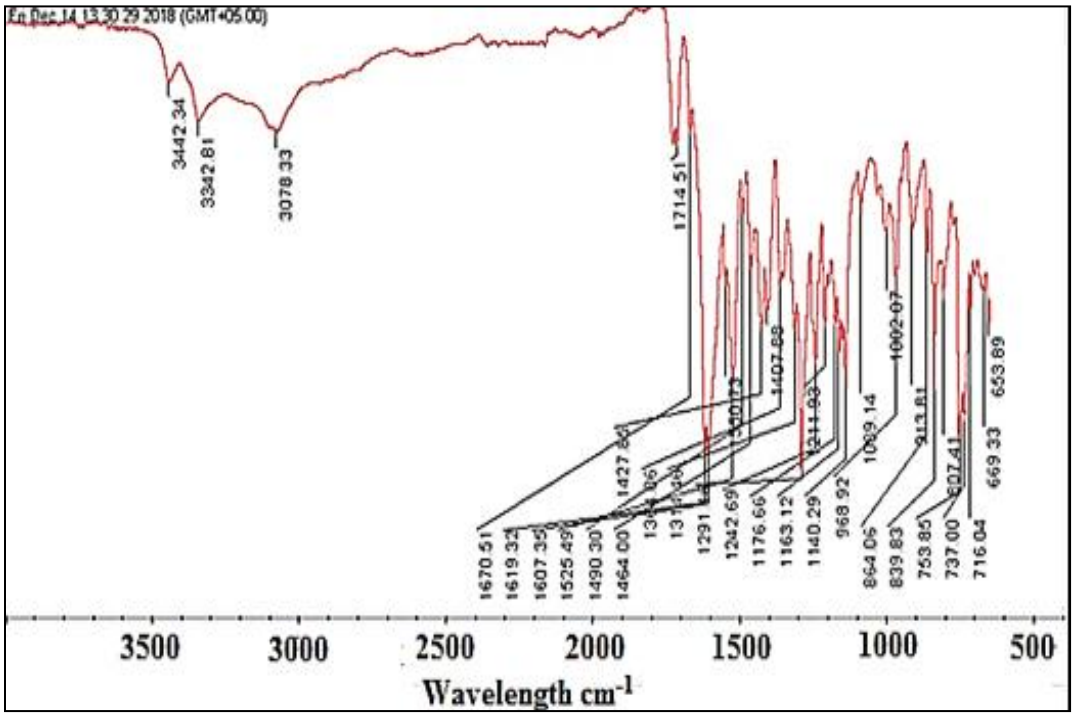


Figure 5 (a). FT-IR Spectrum of BMNMXD

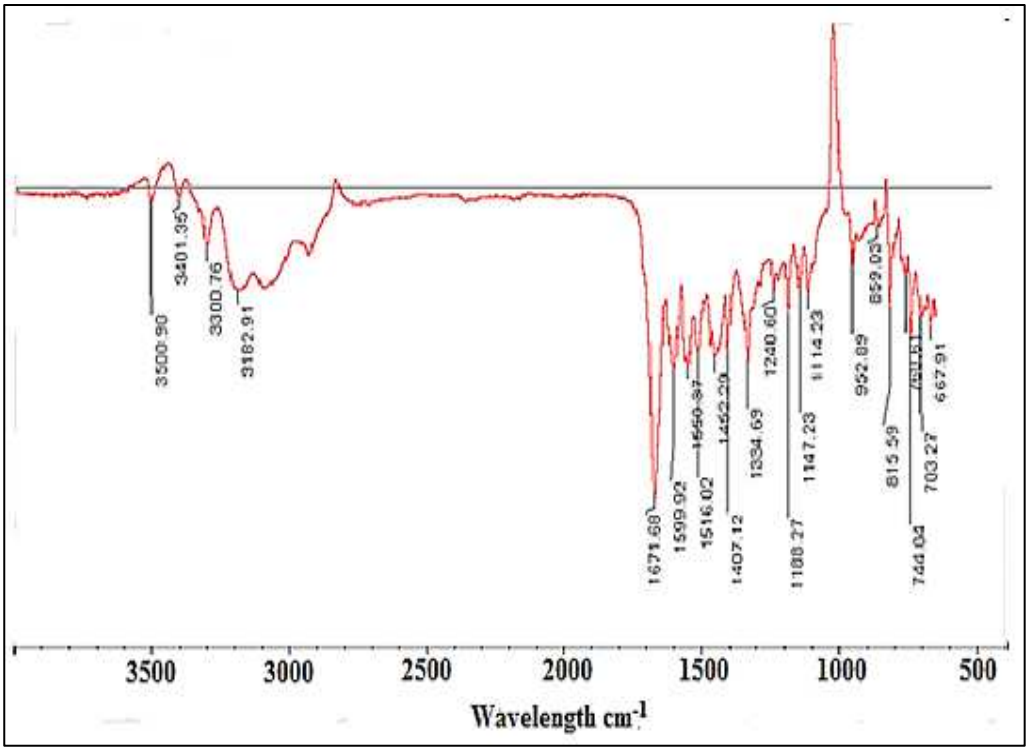


Figure 5 (b). FT-IR spectrum of PMBMNMXD

3.3. Thermal analysis (TGA) of Schiff base resin PMBMNMXD

The thermal analysis of Schiff based resin PMBMHNMXD is shown **Figure 6.**.The Thermal analysis of the sample is show in the figure. Initial weight loss of about 3 % region 50-100 ^{0}C is due to the water in the sample .Between 200 and 390 ^{0}C. The material suffered rapid weight loss (Tmax).

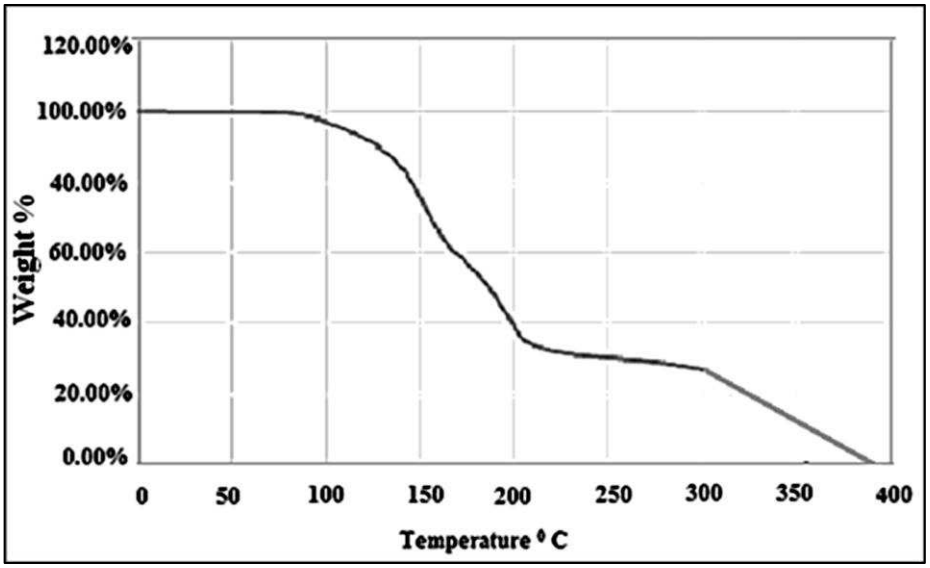
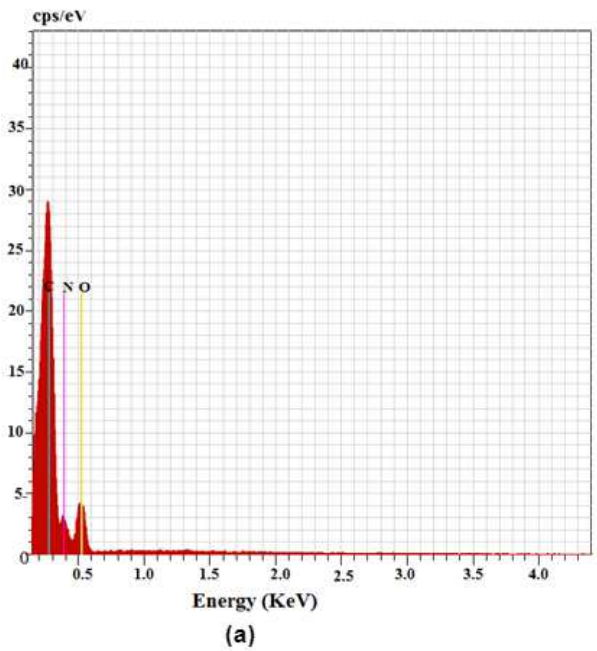


Figure 6.TGA of Schiff Based Resin PMBMNMXD

3.4. Energy-dispersive X-ray (EDS) analysis

EDS spectrum and elemental composition demonstrates the schiif base **BHMNMXD** and schiff based resin **PMBHMNMXD** and Identified the material has mainly composed of carbon and oxygen as a esential material along with N as a constitute in the EDS elemental analysis is shown in **Figure 7** (a) BHMNMXD 51.51 % C, 17.49% O, and 30.99% N (wt.%) and **Figure 7** (b) PMBHMNMXD shows a composition 80.92% C,19.0 % O, and 34.98% N(wt.%) as evidence of successful inter-diffusion and the formation of compound.



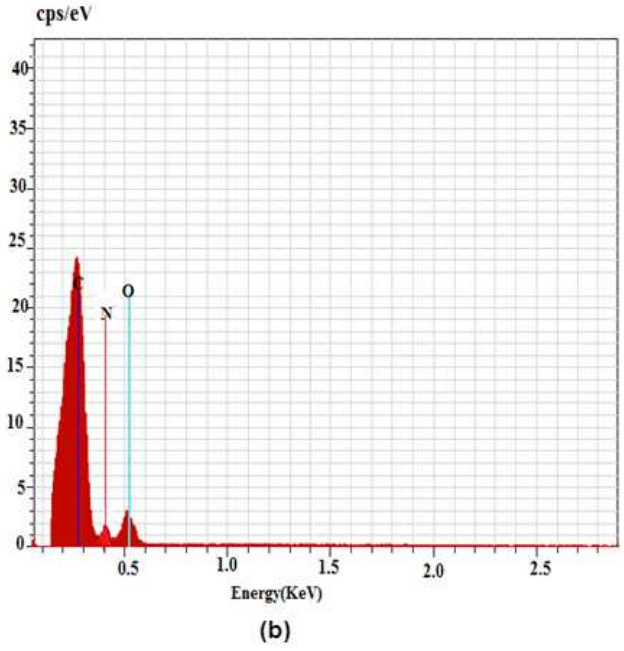


Figure 7 (a). EDS spectrum of BMNMXD **Figure 7** (b).EDS spectrum of PMBMNMXD

3.5. Scanning electron microscopy (SEM) analysis

The synthesized compounds schiff base **BMNMXD** and schiff based resin**PMBMNMXD**were subjected to SEM analysis. **Figure 8 (a),** and **Figure 8**. **(b)** shows SEM images before and after resin formation, The two images present the morphological variation before and after the polycondensation reactions. The topogrphic results The synthesized compounds schiff base **BMNMXD** and schiff based resin **PMBMNMXD** were subjected to SEM analysis. The two images present the morphological variation before and after the polycondensation reactions. The topogrphic results of Schiff based **BMNMXD** particles indicated observable variation from fibrous flower petal shaped, thread like spherical, irregular,longitudional structure to regular laminted structure submerged closed packed spherical surface particles of schiff based resin **PMBMNMXD**,confirming formation of resin

The **Figure 8 (a),** of SEM images represented of Schiff base BMNMXD at magnification × 1000 indicating, the irregular and ‘‘flake” shaped surface. And effective fibrous flower petal shaped structure.The images showing that typical fibrous shape spherical, longitudinal structure. The diameter of Schiff base particles were in the range of 10 micron. In **Figure 8 (b),** SEM images represented of sc resin,PMBMNMXD at a magnification × 500 to1,000 indicating the strong binded merged particles ranged between 10-50 micron.Schiff based resinshowed that most of its particles were consisting of a cluster of closely-packed, sphericaldisplaying uniform average size and close-packed surface.SEM studies provided more accurate clue about the srtucure of polymer.It showed that regular laminted structure which gradually disappeared from the surface of sample where as the surface showed. The images could directly reflect the effect of polymerization,thus resulting in increase homogenous distribution as showed in schiff based resin.

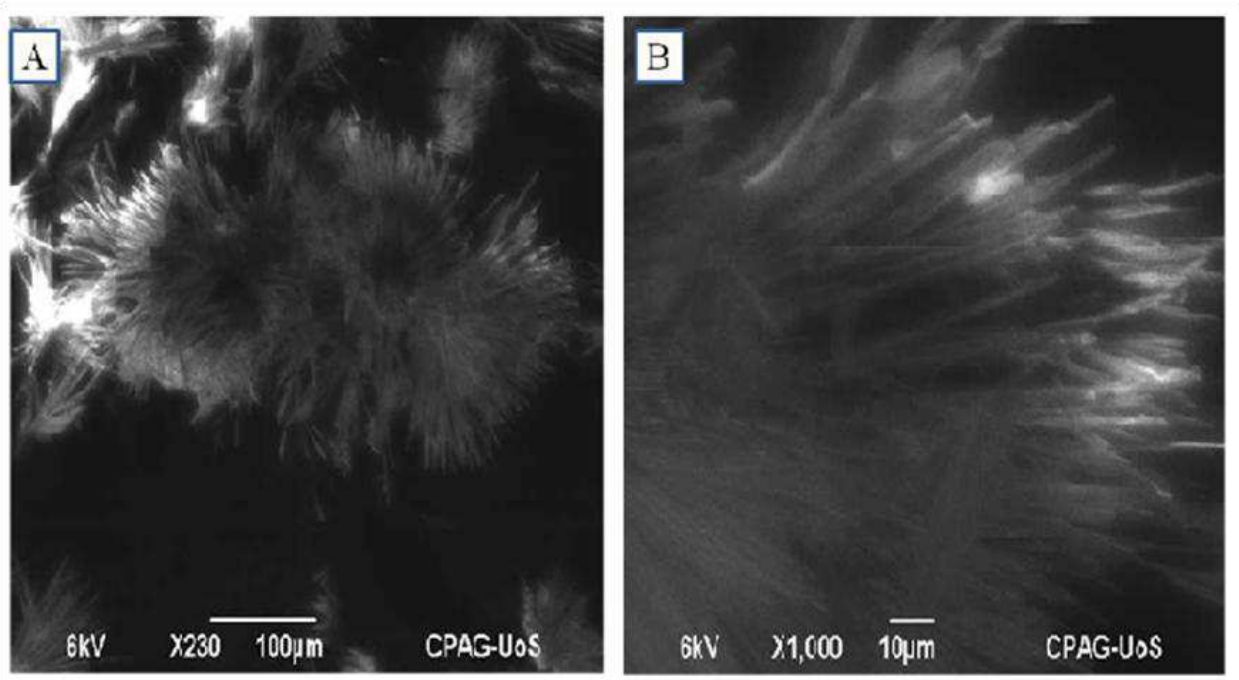


Figure 8. **(a) .**SEM Images of BMNMXD

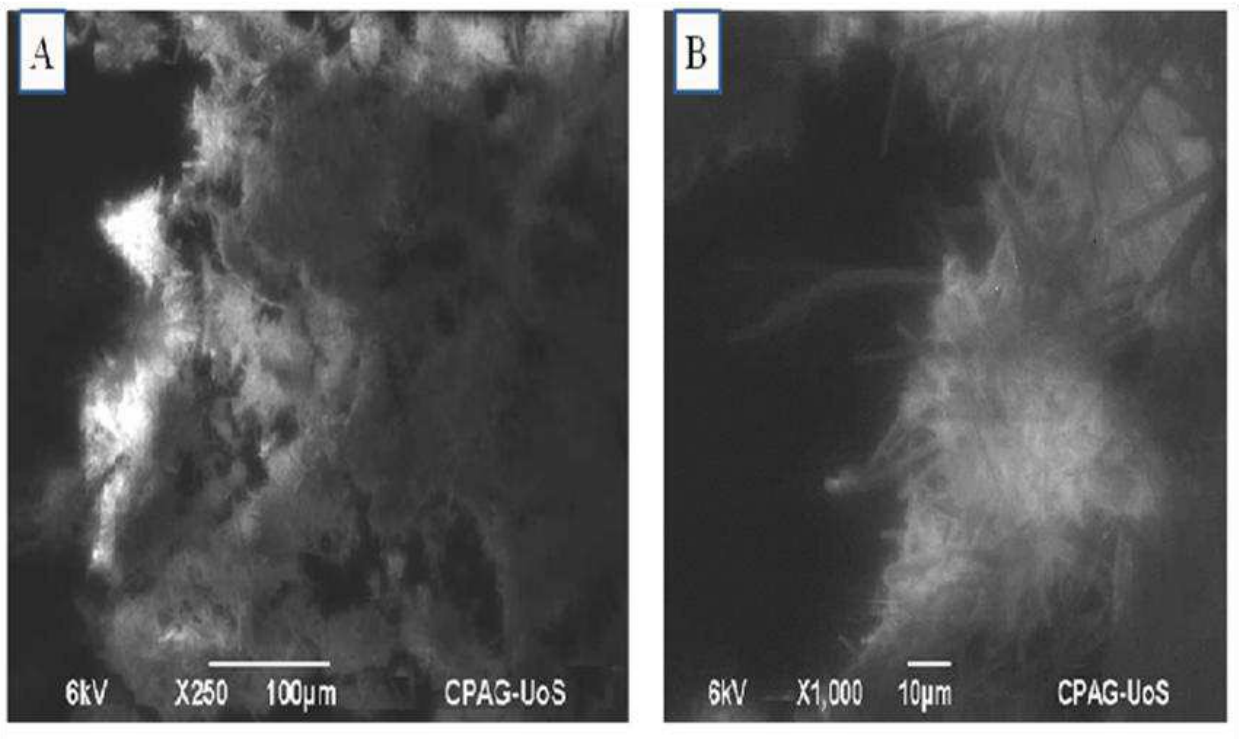


Figure 8 (b). SEM images of PMBMNMXD

3.6. X-ray diffraction (XRD) analysis

In the X-ray diffraction (XRD) **Figure 9.** Showed that the planes with peaks at 2θ, the peaks 2θ = 12.1 and11.4 are associated with the (020),(110) planes).It has displayed the crystallographic evaluation of Schiff base BMNMXD, and resin PMBMNMXD. The black line in diffractogram represent Schiff base BMNMXD**,** 2θ at 12.1, 19.1, 21.1 and 12.1 the red one represents its resin PMBMNMXD displaying 2θ at11.4, 15.9, 24.6 and 23.4.The red lined diffractogram of PMBMNMXD showed sharp and intense peaks compared to BMNMXD,2θ at11.4, 15.9, 24.6 and 23.4.The peaks indicated crystallinity, showing the samples are crystalline in nature, and are associated with the (020), (200),(011) and (310) planes, respectively. The diffractogram were found in agreement with JCPDS card no: 13755-38-9 (The powder diffraction file (PDF) for Orthorhombic structure.

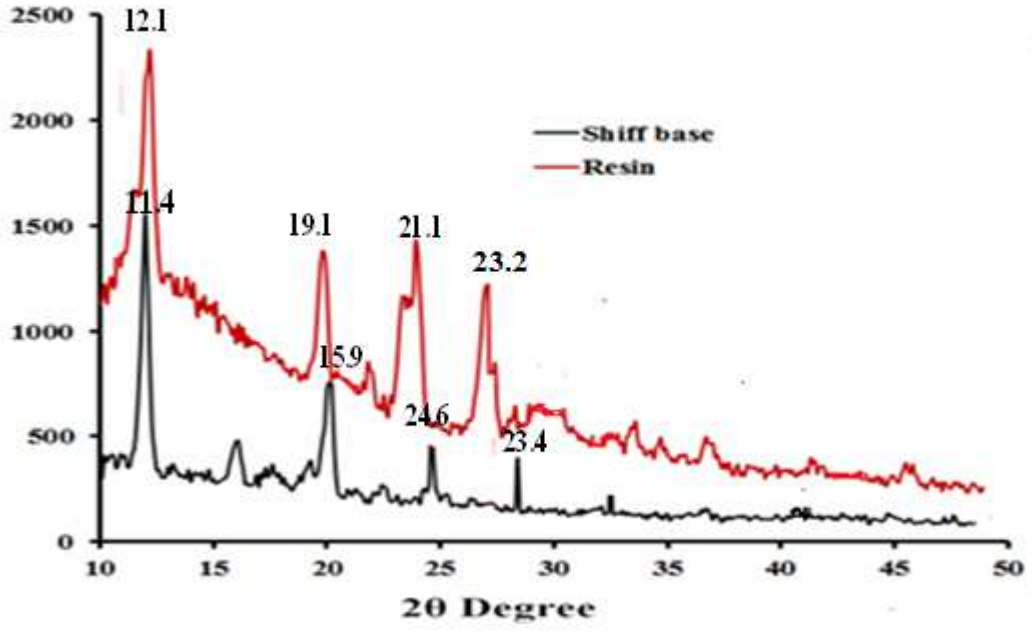


Figure 9. .XRD diffractrogram of BNMXD (black) and PMBNMXD (red).

3.7. Metal ion uptake studies of Schiff base (BHNMXD) and resin (PMBHNMXD) by batch method

3.7.1. Effect of contact time

To study the equilibrium time in the range of 10–50 min, 20mg of PMBMHMXD was dissolved in 25 ml of distilled water in the flask, stirred for 10-15 minutes and 20 ml of (10µg/ml) of Cr (VI) and Ni (II) solutions were also added were used with 100 rpm shaking speed. The Cr (VI) ions exhibit enhanced % adsorption as compared to Ni (II) show in **Figure 10**.The rate of uptake of resins PMBMHMXD in the initial stage was found to be fast (85% Ni and 90% Cr), establishing equilibrium within 60 min. The results showed that as the The Cr (VI) extraction was better than Ni (II).However, it is observed that effect of contact time in batch method of PMBMHNMXD by batch method observed that the removal capacity (qe) of the % Adsorption of Cr (VI) and Ni (II)adsorbent increase with an increase in the time equilibrium.

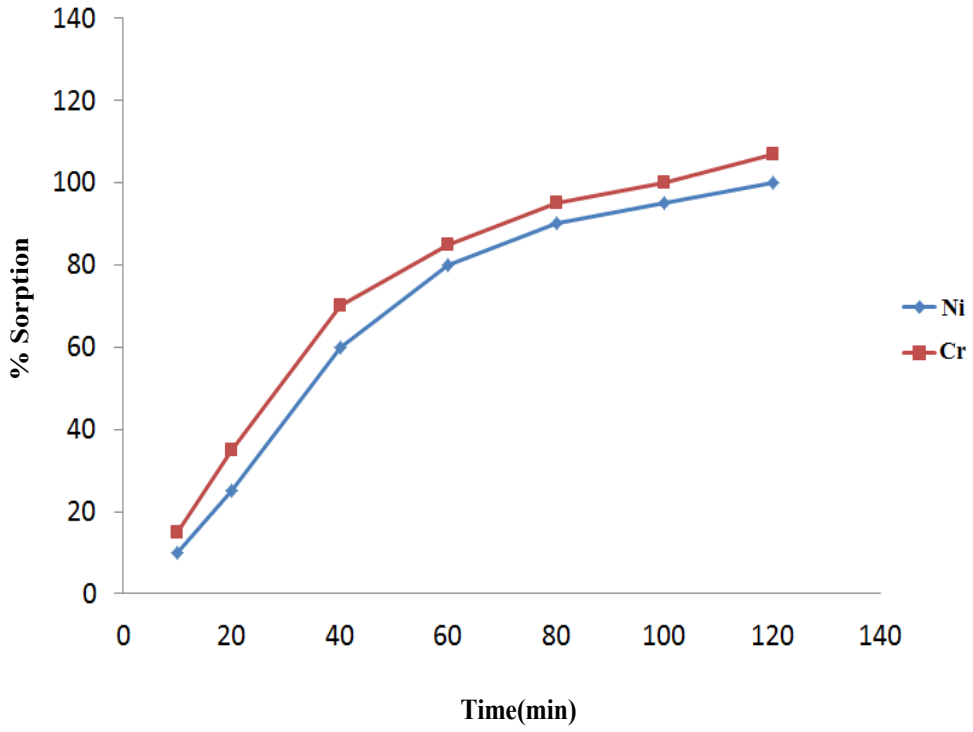


Figure 10. Effect of contact time on removal of chromium and nickel metal ions. Conditions: Ni(II) and Cr(VI) solutions at 10lg/mL concentration, time 60min, adsorbent dose 20mg and pH 6.0.

3.7.2. Effect of temperature

The amount of 20mg of BHMNMXD was dissolved in 25 ml of distilled water in the flask, stirred for 10-15 minutes 20 ml of (10µg/ml) of Cr(VI) and Ni (II) solutions were also added were used with 100 rpm shaking speed, for 20 ml of (10µg/ml) of Cr(VI) and Ni (II) solutions. The Ni (II) ions show enhanced % adsorption as compared to Cr (II) Figure 9:.The rate of uptake of resin PMBMHNMXD in the initial stage was found to be fast (85% Cr(VI) and 97 % Ni(II) establishing equilibrium within 80 min. The Ni (II) extraction was better than Cr(VI) Temperature has positive effect on adsorption and the q value was found to increase with increase in temperature.

The increased flexibility of the polymeric chains and high thermal mobility of Cr(VI) and Ni (II) ions at higher temperature improve their effective interactions Moreover, the polymeric resin structure opens up more adsorption sites become exposed for interaction with the targeted ions at higher temperature. However, it is observed that the removal capacity of the % Adsorption of Cr(VI) and Ni (II)adsorbent increase with an increase in the temperature shown in **Figure 11**.

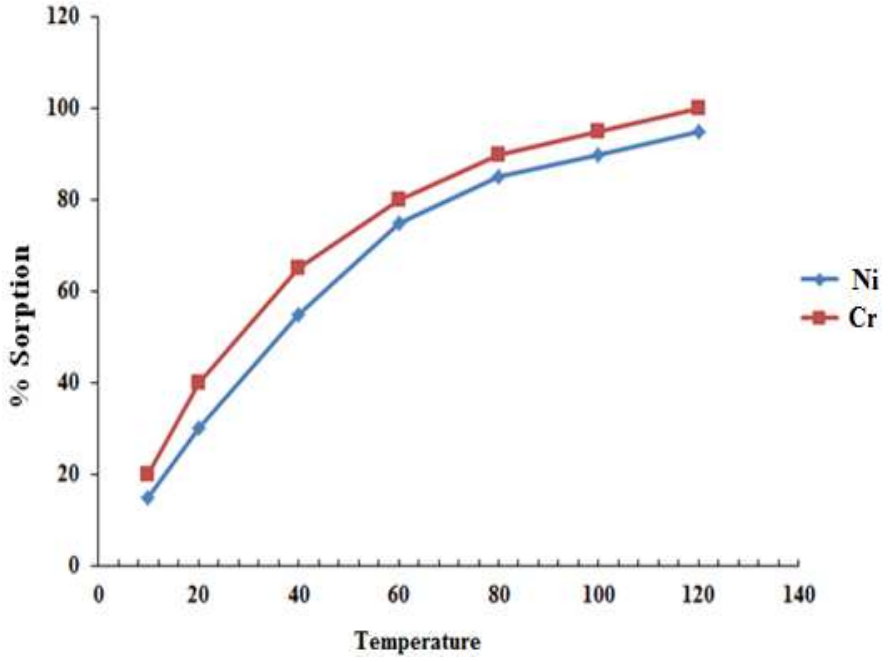


Figure 11. Effect of temperature on the chromium and nickel ions. Conditions: Ni(II) and Cr(VI) solutions with (10lg/mL) concentration, temperature 60˚C, adsorbent dose 20mg and pH 6.0.

3.7.3. Effect of pH on adsorption

The effect of PH studies of resins PMBMNMXD was observed that greater basicity of azomethine nitrogen at pH values is one of the reasons for the complexes to remove high % of metal ions at elevated pH. The % sorption of both the metal ions decreased with increase in pH and precipitation of metal ions as hydroxides resulted. On lowering the pH, protonation of C=N group occurred. The % sorption was higher in the Ni (II) ions as compared to Cr (VI) ions. The amount of adsorption of Ni (II) and Cr(VI) was examined by using buffers ranging pH within (3-6) for Cr(VI) and (4.0 – 9.0) for Ni (II).The resins PMBMNMXD were able to remove 80% of Cr (II) ions and 90% of Ni (II) ions. **Figure 12** shows an increase in adsorption % upon an increase in the pH of solution.

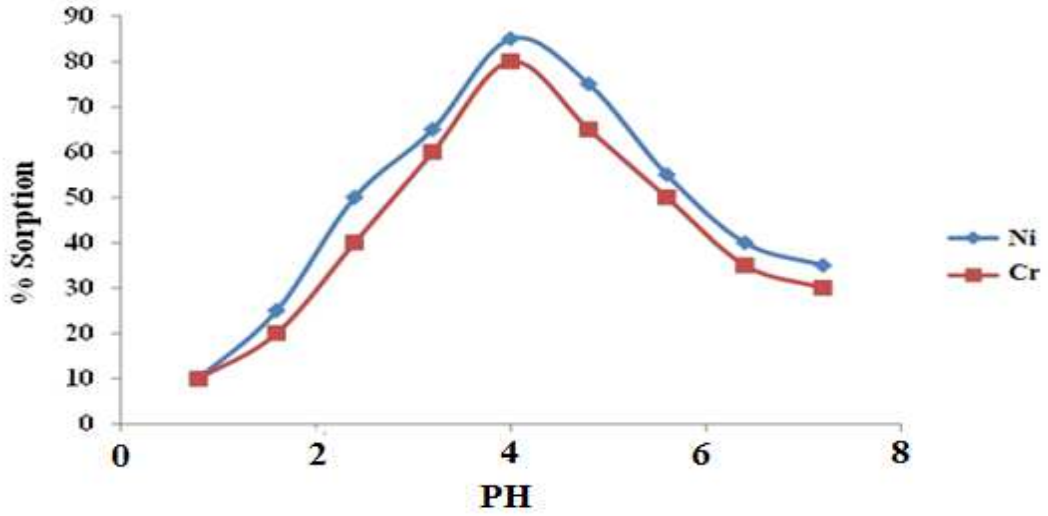


Figure 12. Effect of pH on uptake of nickel and chromium metal ions. Conditions: Ni(II) and Cr(VI) at 10lg/ mL concentration, temperature 60 ˚C, adsorbent 20mg

3.7.4. Effect of adsorbent amount

The resin (20mg) was dissolved in 10 ml of deionized water in the flask, stirred for 10-15 minutes 10ppm concentration Cr(VI) solution were also added, were used with **100 rpm** shaking speed. The material in the flask was filtered, and the resin was washed with deionized water. Then 2mL of 1,5-diphenyl carbazide (CA complexion agent) was added to each solution and analyzed via UV absorption. The effect of adsorbent dose was studied by different initial concentrations of Cr(VI) including viz.20mg, 40mg, 60mg, 50mg, 100mg, **Figure 13** summarizes the results, an increase in removal as the amount of adsorbent is increased, reaching 99% at 100mg Initially, with an increase in the adsorbent dose up to 20 mg/L, the percentage of Cr (II) removed increases 99% at 100mg.

The Tables 2 and 3 summarize our optimization experiments for determining the best conditions for the removal of Cr(VI) and Ni(II). it is observed that the removal capacity (qe) of the adsorbent decreases with an increase in the amount of adsorbent shown in **Figure 13**.

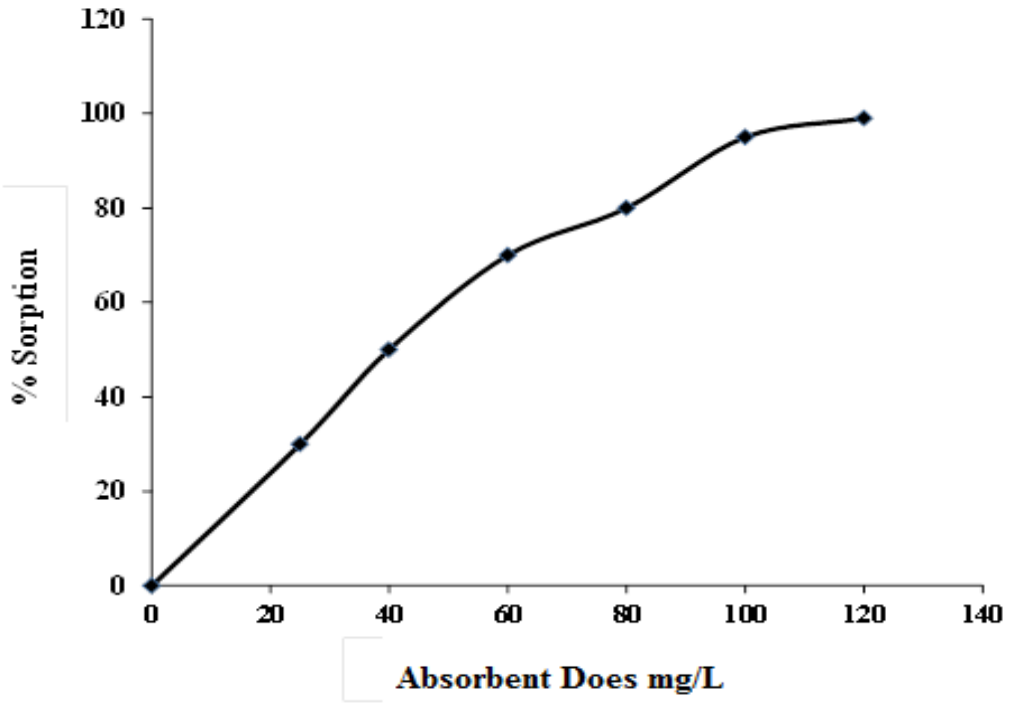


Figure 13.. Effect of adsorbent amount on the removal of Cr(VI) Conditions: 60min, pH 6, adsorbent dose 20mg at 50 ˚C.

Table 2. Optimum condition for Ni(II) adsorption. 100mg/L Ni(II).

Parameters	Variation range	Optimum value	q_e (mg/g)	Absorption efficiency %
Absorption amount (g)			20 mg	
pH	3-6	50		90
Time	0-120	60		85
Temperature	0-140	80		87
Absorbent dose	20-120	89		98

Table 3. Optimum condition for Cr(VI) adsorption. 100mg/L Cr(VI).

Parameters	Variation range	Optimum value	q_e (mg/g)	Absorption efficiency %
Absorption amount (g)			20 mg	
pH	4.0-9.0	40		80
Time	0-120	80		90
Temperature	0-140	98		99
Absorbent dose	20-120	90		99

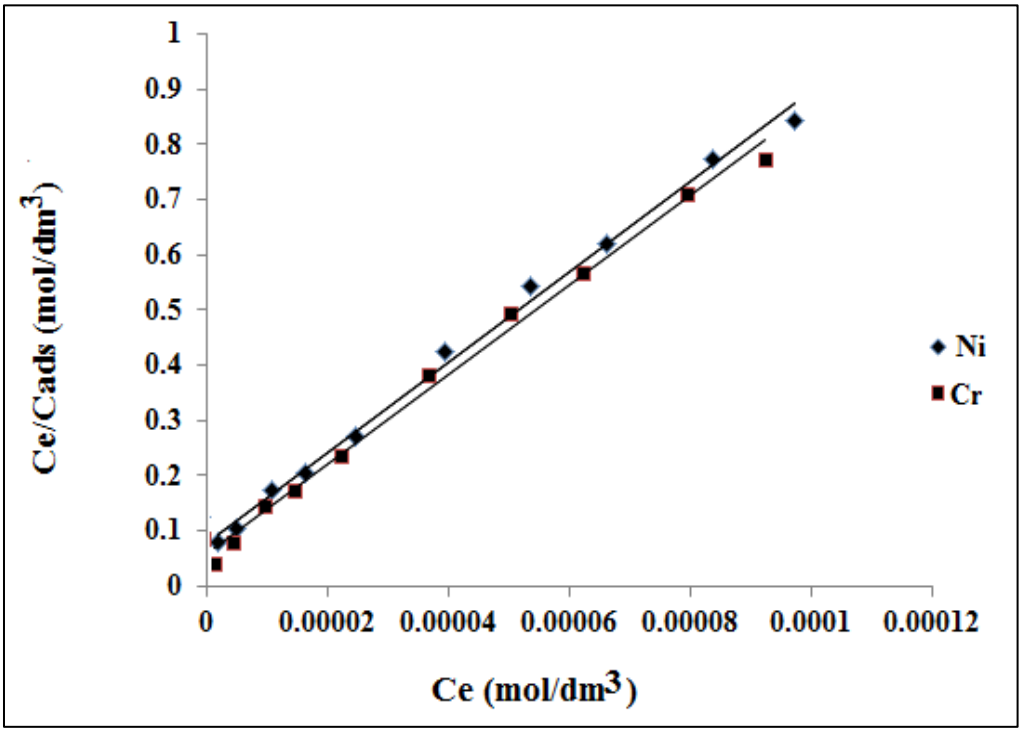
3.8. Adsorption Isotherms Studies

Adsorption is the collective phenomenon of a mass transfer process of an adsorbate at the boundary between solid and aqueous phases. Equilibrium relationships between sorbent and sorbate at constant temperature are described by adsorption isotherms, i.e., the ratio between the amount of solute adsorbed and the residual portion left in the solution at equilibrium. Experimental data is fitted with different isotherm models to evaluate suitability of the model which can be used for designing the process. Adsorption isotherms parameters are usually evaluated to estimate the competence of different types of adsorbent for the adsorption of a particular adsorbate under predefined reaction condition. It helps to choose the most suitable

adsorbent and for the determination of sorbent dosage required for the process. The adsorption data was tested to “Langmuir adsorption isotherm”, “Freundlich isotherm”

3.8.1. Langmuir isotherm

The Langmuir isotherm model is a average for the adsorption of gases into solid adsorbents by the configuration of mono layers. PMBMNMXD represent that the adsorption of chromium and nickel is best described by a Langmuir isotherm based on plots of Ce/Cads against Ce that give a straight line **Figure 14.**



. **Figure 14** langmuir isotherm of the adsorption of Cr(VI) and Ni(II) at different temperatures.

3.8.2. Freundlich adsorption isotherm

The Freundlich isotherm plot is linear for PMBMNMXD as represent in **Figure 15**. The principle of this method is to explore multilayer adsorption and to consider the intensity of adsorption. A plot of Ce/Cads against Ce was linear, suggesting that the data fit very well to a Freundlich adsorption.

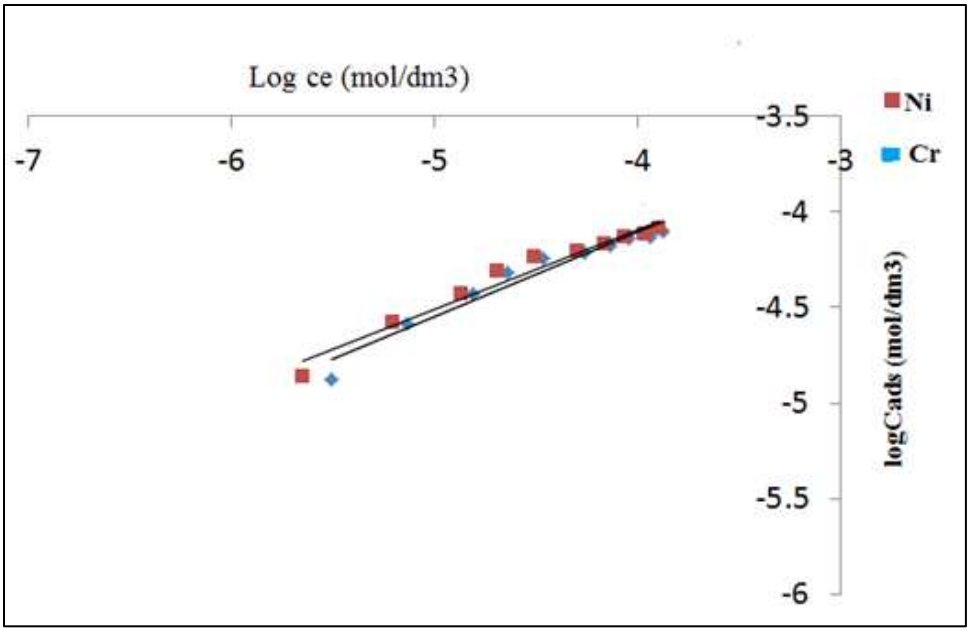


Figure 15. Freundlich isotherm of the adsorption of Cr(VI) and Ni(II) at different temperatures

3.8.3. Adsorption kinetics studies

Adsorption kinetics is mostly used to express the dynamic process of adsorbate concentration and equilibrium adsorption capacity with time in the process of reaction adsorption, which is supportive to understand the adsorption performance of the adsorbent and the adsorption mechanism of the adsorption process. The experimental data of Schiff based resins was tested for two kinetic models, i.e. the pseudo first-order and pseudo second-order kinetic models which have been used extensively to describe the kinetics of metal ion adsorption processes.

3.8.4. Pseudo-first-order reaction

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The model is defined as the effect of time on the adsorption of Cr(VI) was further investigated by using pseudo first order and pseudo second order Kinetic on the adsorbent. The linear plots of log (qe – qt) against t (minutes) gives the slope as the rate of reaction, k^1 and intercept of log qe.. The pseudo first order model is expressed in following.

$$\ln (qe - qt) = \ln q_e - k_1 t$$

Where K_1 is pseudo-first order rate constant (min^{-1}) of adsorption and q_e and q_t (mg/g) are the amounts of metal ion adsorbed at equilibrium and time t (min) The plot for the resin is shown in **Figure 16**. The relationship is not linear and thus further analysis was performed.

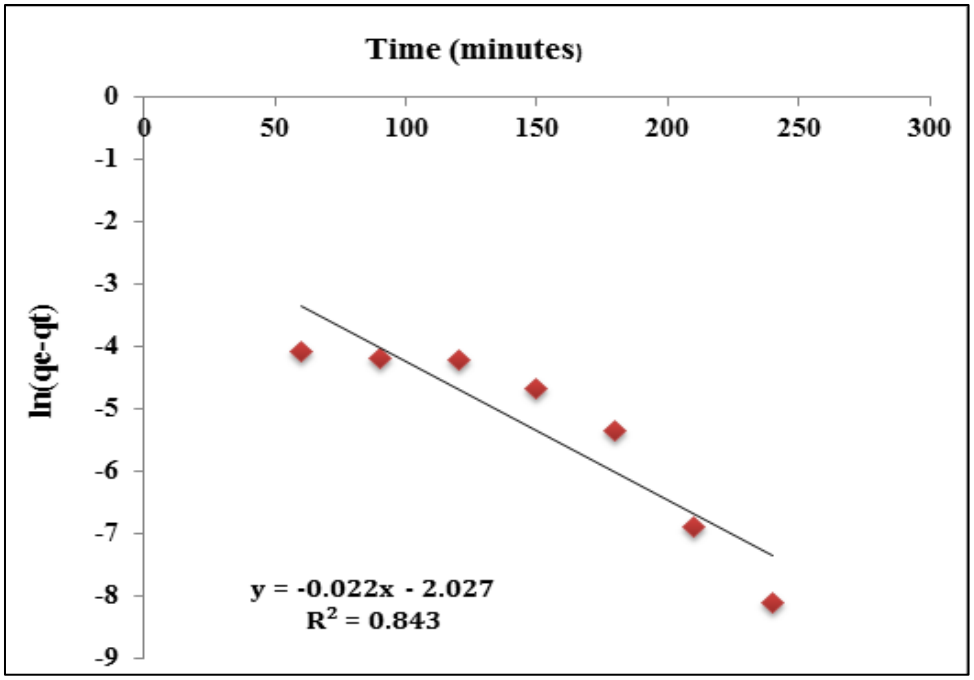


Figure 16. Pseudo-first-order plot for the adsorption of Cr(VI) by PMBMNMXD

3.8.5. Pseudo-second-order reaction

The pseudo-second-order equation predicts the behavior over the whole range of the adsorption process and appears to be controlled by the chemical sorption mechanism as the rate controlling step. The pseudo second order kinetic model describes the rate of adsorption, which correlates with the squared difference between the number of the equilibrium binding sites to that of the occupied sites on the adsorbent [41].

Second-order kinetics follows the model

$$\frac{t}{q_t} = \frac{t}{K_2 qe^2} + \frac{t}{q_e}$$

The **Figure 17,** shows the values of k_2 and qe (cal) calculated by the intercept and slope of the plot t/qt against time (min). The coefficient value (R^2) in the pseudo-second-order kinetic model of PMBMNMXD was 0.999. The relationship was linear when a second- order kinetic model was used, suggestive that that this mechanism is operative.

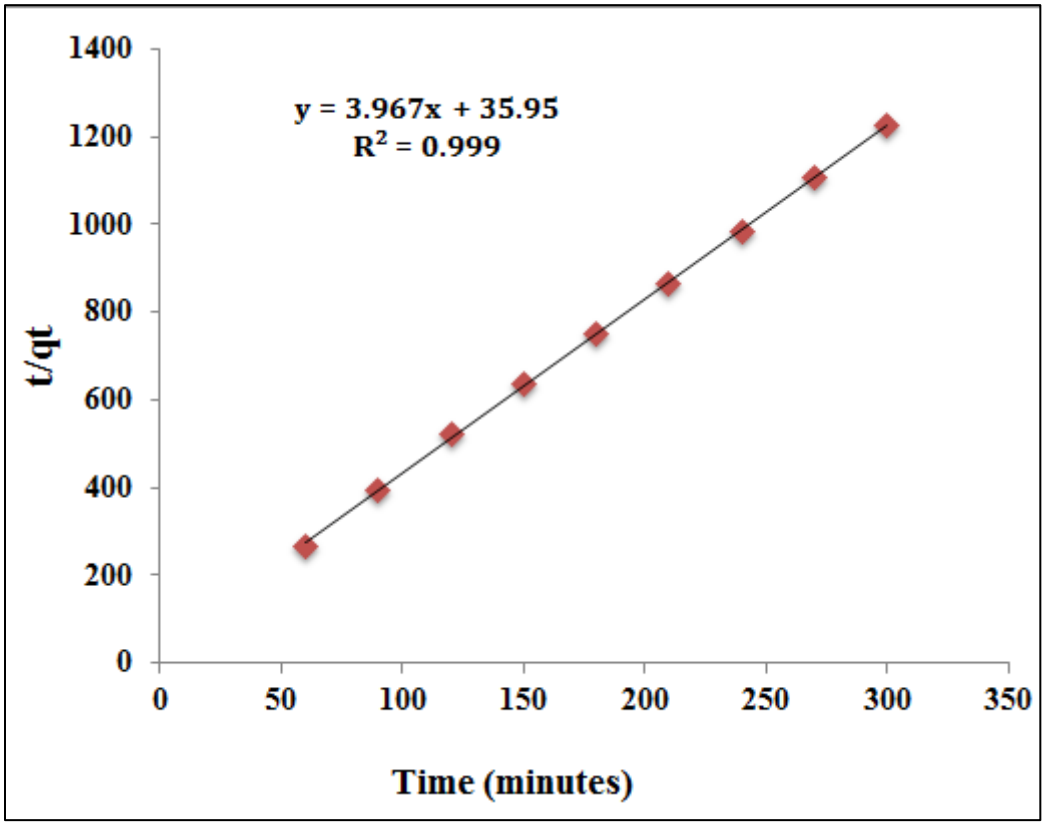


Figure 17. Pseudo-second-order plot for the adsorption of Cr(VI) with PMBMNMXD.

3.8.6. Application of PMBMNOPhen for elimination of Cr(VI) and Ni(II) ions from real water samples

The removal of Cr (VI) and Ni(II) from a range of real water samples was carried out.

The **Table 4**.shows the % adsorption of chromium (VI) and nickel (II) in samples from different agriculture land of Sindh province, Sanghar, Tando-Adam, Kotri, and Jamshoro. The synthesized material PMBMNMXD was able to remove 97% of Cr (VI) and 93% Ni(II) ions in the water sample from Sanghar.

The PMBMNMXD eliminated 99% of Cr (VI) and 98% Ni(II) ions from the water sample from Kotri. The resin PMBMNMXD was able to eradicate 95% of Cr (VI) and 98% Ni(II) ions in the water sample from Jamshoro. The resin PMBMNMXD was highly efficient to eliminate 92% of Cr (VI) and 91% Ni(II) ions of the water sample from Nawabshah.

Table 4. % Adsorption and % recovery of Cr(VI) and Ni(II) from real water samples by polymeric resin PMBMNMXD

Sample Collected From agriculture land of different cities of Sindh, Province (Pakistan)	Amount of Cr (VI) and Ni(II) ions in surface water sample "µgL'	Resin PMBMNMXD			
		Cr (VI)		Ni(II)	
		% Sorp	% Recover	% Sorp	% Recover
Sanghar	0.4 ±0.3	97.0 ±0.4	95.0 ±0.2	93.0 ±0.5	92.0 ±0.4
Kotri	0.5±0.2	99.0±0.2	96.0±0.3	98.0±0.6	90.0±0.6
Jamshoro	0.8 ±0.6	95.0±0.6	97.0 ±0.3	98.0 ±0.4	94.0 ±0.5
Nawabshah	0.6±0.4	92.0±0.4	95.0 ±0.5	91.0 ±0.6	92.0±0.3

4. Conclusion

We synthesized BMNMXD and converted after condensation to resin form PMBMNMXD. The synthesized material was characterized by CHN analysis, FT-IR, TGA, EDS, SEM, and XRD. The FT-IR spectrum of PMBMNMXD strong band at1671 cm^{-1}.The 1 cm in resin toward higher frequency confirmed the formation of resin. EDS spectrum showed that Identified the material has mainly composed of carbon and oxygen as a esential material along with N as a constitute.

The SEM analysis showed the fibrous shape spherical, longitudinal structure. most of its particles were consisting of a cluster of closely-packed, sphericaldisplaying uniform average siz.and XRD analysis indicated crystallinity, showing the samples are crystalline in nature.

The synthesized Schiff based resin used for adsorption of Cr (II) and Ni(II) from aqueous solution was studied at various temperatures using batch model experiments. The adsorption of Cr (II) and Ni (II) were studied. Optimum conditions were used for different parameters such as pH, concentration of the solution; effect of time, effect of Temperature and effect of does study. The sorption results were used to examine different sorption isotherms like, Langmuir, Freundlich and kinetic studies such as, pseudo first order kinetics and pseudo second order kinetics. The *slope* and *linear plot* was used to evaluate the sorption isotherms. The PMBMNMXD eliminated 99% of Cr (VI) and 98% Ni(II) ions from the water sample from Kotri. The resin PMBMNMXD was able to eradicate 95% of Cr (VI) and 98% Ni(II) ions in the water sample from Jamshoro. The resin PMBMNMXD was highly efficient to eliminate 92% of Cr (VI) and 91% Ni(II) ions of the water sample from Nawabshah.

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Author statement

All authors contributed to the study conception and design. The material preparation data collecting and investigation were performed by Dr. Moina Akhtar, Dr. Aamna Balouch and Dr. Khalid M. Khan. The first draft of the manuscript was written by Dr. Nasira Liaquat Rajput. All authors read and approved the final manuscript.

Disclosure statement

No potential conflict of interest was reported by the authors.

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FIGURE CAPTION

Graphical Abstract
Figure 1. Reaction scheme to form Schiff base BMNMXD.
Figure 2. Reaction scheme of Schiff base resin PMBMNMXD
Figure 3. Synthesized Polymeric Resin
Figure 4. Thermostat shaker used for metal up takes study by batch methodFigure 5.. (Top) FT-IR Spectrum of BMNMXD (Bottom) FT-IR spectrum of resin PMBMNMXD
Figure 6.TGA of Schiff Based Resin PMBMNMXD
Figure 7 . (a) EDS spectrum of BMNMXD
Figure 7 . (b) EDS spectrum of PMBMNMXD
Figure 8 (a) .SEM Images of BMNMXD
Figure 8 (b). SEM images of PMBMNMXD
Figure 9. .XRD diffractrogram of BHNMXD (black) and PMBHNMXD (red).
Figure 10. Effect of contact time on removal of chromium and nickel metal ions. Conditions: Ni(II) and Cr(VI) solutions at 10lg/mL concentration, time 60min, adsorbent dose 20mg and pH 6.0.

Figure 11. Effect of temperature on the chromium and nickel ions. Conditions: Ni(II) and Cr(VI) solutions with (10lg/mL) concentration, temperature 60˚C, adsorbent dose 20mg and pH 6.0.

Figure 12. Effect of pH on uptake of nickel and chromium metal ions. Conditions: Ni(II) and Cr(VI) at 10lg/ mL concentration, temperature 60 ˚C, adsorbent 20mg

Figure 13.. Effect of adsorbent amount on the removal of Cr(VI) Conditions: 60min, pH 6, adsorb- ent dose 20mg at 50 ˚C.

Figure 14 langmuir isotherm of the adsorption of Cr(VI) and Ni(II) at different temperatures.
Figure 15. Freundlich isotherm of the adsorption of Cr(VI) and Ni(II) at different temperatures
Figure 16.Pseudo-first-order plot for the adsorption of Cr(VI) by PMBMNMXD
Figure 17. Pseudo-second-order plot for the adsorption of Cr(VI) with PMBMNMXD.

Table 1. CHN elemental microanalysis BMNMXD and PMBMNMXD

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Table 3. Optimum condition for Cr(VI) adsorption. 100mg/L Cr(VI).

Table 4. % Adsorption and % recovery of Cr(VI) and Ni(II) from real water samples by polymeric resin PMBMNMXD