Two formaldehyde-based terpolymeric resins (anthranilic acid-catechol-formaldehyde (ACF) and salicylic acid-catechol-formaldehyde (SCF)) have been synthesized by condensing anthranilic acid with catechol and salicylic acid with catechol at $80 \pm 5 ^\circ C$ using dimethylformamide as a solvent. The resins were characterized by spectral analysis using Fourier-transform infrared (FTIR) spectroscopy. The physical-chemical properties of the resins have been studied. The exchange behavior of various metal ions, namely, $\text{Cd}^{2+}$, $\text{Cr}^{3+}$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$, towards the synthesized resins has been studied depending on contact time and pH. Chelating properties of two resins were pH dependent, and with an increase in pH value from 1 to 5, the exchange capacity of metal ions was increased. The increasing rate of ion-exchange capacity was greater in ACF than that in SCF. $\text{Cd}^{2+}$ showed higher rate of exchange at different time intervals in both cases, ACF and SCF. $\text{Cr}^{3+}$ had higher exchange capacity with pH variation in both resins.

1. Introduction
Over the last years, there has been a growing concern for the immobilization of metal ions introduced into bodies of water and wastewater by increasing human technological activities. It has been established beyond doubt that the ions of heavy metals in the environment (air, soil, and water) pose a serious risk to human health. With the exponential increase in the population, it is essential to govern the release of poisonous heavy metallic ions earlier than getting into the complex ecosystem. Incorporation of the functional group into the polymeric matrix is of great interest in connection with trace concentration of heavy metal ions. Numerous phenolic formaldehyde copolymers have been described to have satisfactory ion-exchange properties. Srikanth et al. mentioned that ion-exchange resins (IERs) are insoluble polymers that contain acidic or primary purposeful groups, and that they have the ability to change counterions inside aqueous solutions surrounding them. An IER is like a small bead with a diameter between 1 and 2 mm [1]. Ion exchange is a popular approach because of its applicability to both preattentation and separation. The attention on this form of chelating resins is because of the fast adsorption of metal ions, better selectivity, and less swelling in contrast to the analogous organic polymers [2]. The uptake behavior of various metal ions, namely, $\text{Ni}^{2+}$, $\text{Cu}^{2+}$, $\text{Zn}^{2+}$, $\text{Cd}^{2+}$, and $\text{Pb}^{2+}$, toward the synthesized resin has been studied depending on contact time, pH, and temperature [3]. Terpolymer resins of o-cresol-urea-formaldehyde had been synthesized in the presence of an acid catalyst with exclusive molar proportions of monomers [4]. Many approaches are available inclusive of chemical precipitation, oxidation, discount, coagulation, adsorption, solvent extraction, and ion exchange for the elimination, separation, and enrichment of trace metals from aqueous solutions. The extraction of metal ions with the usage of a chelating ion-alternate resin is a green analytical method since it does not contain poisonous chlorinated organic solvents, which are mostly used.
in the traditional liquid-liquid extraction method or other methods [5]. Chelating ion-alternate resin has been synthesized by condensing p-hydroxybenzoic acid with formaldehyde by employing resorcinol as a cross-linking agent at 80 ± 5°C and DMF as a solvent, and its ion-exchange ability and selectivity towards Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Pb²⁺ ions have been studied [6]. Kapadia et al. [7–9] prepared ion-exchange resins from numerous phenolic derivatives like salicylic acid, gallic acid, β-resorcylic acid, anthranilic acid, 8-hydroxyquinoline, and hydroquinone using DMF as a solvent. They have studied their anion as well as exchange abilities towards various metal ions. Mubarak and coworkers [10] have analyzed the chelation behavior of the phenolic-formaldehyde polymers toward the trivalent lanthanide metal ions which include La³⁺, Nd³⁺, Sm³⁺, Gd³⁺, and Tb³⁺ through a static batch equilibrium approach at 25°C as a function of contact time, pH, and concentration.

So far, no resin based on anthranilic acid-formaldehyde-catechol in DMF media has been reported with its ion-exchange capacity as a function of contact time and pH. The study described in the present communication processes the synthesis and characterization of absorbents together with the systematic studies of various properties of the ion-exchange resin. The main objective of this research was the preparation of the insoluble part functionalized polymers that can provide in conjunction with more flexible working conditions good stability and high capacity for metal ions. The present paper deals with synthesis and comparative ion-exchange study of a newly synthesized resin obtained by formaldehyde-based ion-exchange resins derived from anthranilic acid, salicylic acid, and catechol.

2. Materials and Methods

2.1. Materials and Reagents. All chemicals used were obtained from Sigma-Aldrich (AR grade). Anthranilic acid, salicylic acid, formaldehyde (37%), and catechol were used as received without further purification. Dimethylformamide (DMF) was used as a solvent for resin synthesis. Acid solution (1 M HCl) is prepared by dissolving an appropriate amount of HCl in distilled water. Solutions of metal ions were prepared by particular metal salts such as cadmium chloride (CdCl₂), ferric chloride (FeCl₃), ferrous sulfate (FeSO₄), magnesium sulfate (MgSO₄), calcium chloride (CaCl₂), and chromium alum [KCr(SO₄)₂·12H₂O]. “Dowex” 50–X8 is used as a reference resin. Glassware was cleaned by soaking in chromic acid overnight. All the other chemical reagents used were of analytical grade. Distilled water was used throughout the research work. Digital pH meter was used for all pH measurements. The GBC AA dual atomic absorption spectrometer fitted with cadmium, chromium, and iron hollow cathode lamps was used to analyze the concentration of metal ions under study. The wavelength was set at 228.8 nm resonance line, the spectral band pass at 0.5 nm, and the measurements were carried out in an air/acetylene flame. Biobase D-580 UV spectrophotometer was used to analyze the concentration of metal ions.

2.2. Resin Synthesis. Two resins were synthesized according to the procedure mentioned by Shah et al. [11]. Salicylic acid (13.5 g, 0.1 mol) was taken in a 250 ml round-bottomed flask and dissolved in DMF solvent (20 ml) to give a clear solution. A solution of catechol (11g, 0.1 mol) in 10 ml DMF was added to the above solution and stirred for two hours. Formaldehyde (0.3 mol as 37%) was added and stirred for an hour. Then, the mixture was refluxed on a water bath at 80 ± 5°C for 2-3 h with constant stirring during which the mixture gelled to a soft mass, which was dark brown in color. The gel was separated from the reaction vessel and cured in an oven at 80–90°C for 12 h. As the carboxylic acid group normally gets decomposed above 100°C, the resin was cured below 90°C. The resulting resin was washed with DMF to remove monomer impurities and finally with deionized water. After completing the washing cycle, the yield of the resin sample was finely ground and passed through a 300 mesh screen and then 500 mesh screen to get a uniform particle size (300–500 mesh). The sieved resin was again washed with water, air-dried at room temperature, and stored in a polyethylene bottle. Anthranilic acid-formaldehyde-catechol resin was synthesized according to the same method mentioned above. The solubility test of resins in different solvents was performed at room temperature and pressure with intermittent shaking. It was found to be nonmelting and insoluble in almost all common organic solvents like acetone, ethanol, DMF, chloroform, etc., and also in acids and alkaline of higher strength (up to 4 M). These sieved resins were characterized using different instrumental techniques and used for all the experiments during the research period. The resin sample was converted into the H⁺ form by the following method. Resin samples having uniform particle size (300–500 mesh) were equilibrated with 1 M HCl solution for 24 h and washed with deionized water till it was free from chloride by testing with silver nitrate solution. This H⁺ form of the resin was used for further studies. The batch equilibrium method was adopted to study the ion-exchange properties.

2.3. Instrumentation. Infrared spectra of the synthesized resin samples had been scanned in KBr pellets on an FTIR spectrophotometer (Thermo Scientific model: NICOLET iS10). The resolution of the spectrometer is 0.4 cm⁻¹, and the spectral range is 4800 to 450 cm⁻¹. A temperature-controlled water bath shaker was used for batch sorption process.

2.4. Batch Sorption Experiments. Effect of contact time and pH on the sorption of metal ions into both resins was studied by the batch technique. To study the effect of contact time, the H⁺ form of accurately weighed (0.250 ± 0.001 g) dry resin samples was taken in different glass stoppered bottles and equilibrated with buffer solutions of desired pH value for 12 h. After decanting the buffer solution, 50 ml (0.02 M) metal ion solution of the same pH was added. The amount of unabsorbed metal ions was determined by means of an atomic absorption spectrophotometer at fixed time intervals. To study the effect of pH on the metal ion uptake, it is necessary to buffer the resins and the solutions used.
Different sets of accurately weighed (0.250 ± 0.001 g) dry resin having uniform particle size (300–500 mesh) were equilibrated with buffer in different stoppered bottles for 12 h, so that resins attained the desired pH value. After 6 h, buffer solutions were decanted, and 50 ml of 0.02 M metal ion solutions of varying pH from 3 to 6 were added. Metal ion solutions were equilibrated at room temperature (30 ± 2°C) for 12 h with intermittent shaking. After 24 h, the solutions were filtered to separate the resin and solution. The pH of the filtrate was measured, and it was found that pH remains stable throughout the experiment (±0.2). The metal ion concentrations in the supernatants were determined using a Perkin-Elmer model 3100 atomic absorption spectrophotometer, and the amount of each metal ion adsorbed was calculated from the difference between its initial and equilibrium concentrations. The ion-exchange capacity was calculated by using the following equation:

\[ q = \frac{(C_0 - C_e)V}{M} \times 1000, \]  

where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations (mg/dm³) of the metal ion in the solution, \( V \) is the volume (cm³), and \( M \) is the weight (g) of the resin.

3. Results and Discussion

Two terpolymeric resins were synthesized by using salicylic acid, anthranilic acid, and catechol and formaldehyde as a cross-linking agent: one is the anthranilic acid-catechol-formaldehyde (ACF) resin and the other one is the salicylic acid-catechol-formaldehyde (SCF) resin. Comparison of sorption behavior in both resins was studied with the “Dowex” 50-X8 resin as reference (Figures 1 and 2).

3.1. Properties of the Resins. Both synthesized resins were in solid form, and their particle size was 0.30–0.50 mm. ACF and SCF were dark brown in color, and SCF was darker than ACF. The melting points of both ACF and SCF resins were 222–225°C and 195–200°C, respectively. The solubility test of resins in different solvents was performed at room temperature and pressure with intermittent shaking, and it was found to be nonmelting and insoluble in almost all common organic solvents like acetone, ethanol, benzene, DMF, and chloroform.

3.2. Spectral Characterization of Resins (FTIR). The FTIR spectrum of the ACF resin is exhibited in Figure 3. The band appearing at 3350.2 cm⁻¹ is due to NH-stretching vibration of the amino group. The medium band at 2900.1 cm⁻¹ is due to the C-H stretching of the methylene group. The strong band at 1652.1 cm⁻¹ may be assigned to C=O stretching vibration of the carbonyl group present in the resin [12]. The weak band at 1372.8 cm⁻¹ is due to C-O-H bending of the aromatic–OH group. The strong band appearing at 1207.9 cm⁻¹ can be assigned to C-N stretching vibration of Ar-NH₂. The medium band at 810.9 cm⁻¹ is due to the C-H bending of the 1, 2, 3, 4-tetrasubstituted benzene ring. The C-H bending of polyethylene–(CH₂) bridges is established by the presence of the medium band at 670.8 cm⁻¹.

The FTIR spectrum of the SCF resin is exhibited in Figure 4. The O-H stretching of the phenolic group is established by the presence of a strong band at 3365.2 cm⁻¹. The medium band at 2910.5 cm⁻¹ is due to the C-H stretching of the methylene group. The presence of a strong medium band at 1630.8 cm⁻¹ is due to the C=O stretching of the aromatic acid group. The C-H deformation of the methylene group is established by the weak band at 1439.5 cm⁻¹, and the weak medium band at 1384.2 cm⁻¹ is due to C-O-H bending of the aromatic–OH group. C-H bending of the 1, 2, 3, 4-tetrasubstituted benzene ring is established by the medium band at 810.7 cm⁻¹. The medium band at 670.8 cm⁻¹ is due to the C-H bending of polyethylene–(CH₂) bridges.
3.3. Ion-Exchange Capacity of ACF and SCF. Calculated exchange capacities of metal ions (Cd$^{2+}$, Cr$^{3+}$, Ca$^{2+}$, and Mg$^{2+}$) for Dowex 50-X8, ACF, and SCF resins are plotted against different time intervals and are illustrated in Figures 5–7, respectively. The exchange of metal ions on resins is time dependent, and it varies for different metal ions. In all three resins, Cd$^{2+}$ shows the highest exchange capacity rather than the other metal ions. The exchange capacity of Cr$^{3+}$, Ca$^{2+}$, and Mg$^{2+}$ shows deviation in different ways for three resins. As compared to the Dowex 50-X8 resin, both synthesized ACF and SCF resins have low exchange capacity with the above metal ions. The graph shows that the SCF resin is more effective for Cd$^{2+}$ and Ca$^{2+}$ than the ACF resin, and the ion-exchange rates of metal ions are varying as follows:

**Dowex 50-X8:** Cd$^{2+} >$ Ca$^{2+} >$ Cr$^{3+} >$ Mg$^{2+}$

**ACF:** Cd$^{2+} >$ Ca$^{2+} >$ Mg$^{2+} >$ Cr$^{3+}$

**SCF:** Cd$^{2+} >$ Ca$^{2+} >$ Mg$^{2+} >$ Cr$^{3+}$

Metal removal ions from an aqueous solution by sorption are strongly dependent on pH of the solution which influences the surface charge of the sorbent. Chelating ligands form complexes with various metal ions in specific pH conditions. Therefore, the synthesized resin has been used to study the effect of varying pH on its chelating ability to various metal ions. The results of the exchange capacity depending on the pH...
for different metal ions are presented in Figures 8–10. In 2006, Singh and Srivastava [13] have stated that the pH of the solution and the pH affect the surface charge of the sorbent. Chelating ligand forms complexes with various metal ions at specific pH conditions. The synthesized resins are used to study the effect of variation in pH on the resin towards various metal ions. The results show that exchange capacity of metal ions was increased with an increase in pH up to a certain value (pH = 1 to 5). The maximum adsorption for Cd$^{2+}$, Cr$^{3+}$, Ca$^{2+}$, and Mg$^{2+}$ took place at pH 5 in three resins. The base resin structure is important in physical absorption of metal ions by the different copolymers of the resin. From the results, it can be viewed that the metal ion-exchange rate is faster at the beginning and then slows down. These occur due to less available site (group) present in the resin. It results in a slower rate of exchange. Figures 8 and 9 show the rate of exchange of the metal ion of the synthetic resin.

The maximum adsorption for Ni$^{2+}$, Cu$^{2+}$, and Pb$^{2+}$ took place at pH 6, and for Zn$^{2+}$ and Cd$^{2+}$, it was at pH 5.5. The selectivity order for metal ions is Cu$^{2+}$ > Zn$^{2+}$ > Pb$^{2+}$ > Ni$^{2+}$ > Cd$^{2+}$, and an increase in pH increases the negatively charged nature of the sorbent surface. This leads to an increase in the electrostatic attraction between positively charged metal ions and negatively charged sorbent, and results in an increase in the adsorption of metal ions. The decrease in the removal of metal ions at a lower pH is due to the higher concentration of H$^+$ ions present in the reaction mixture which competes with the metal ions for the sorption sites on the sorbent surface. Meanwhile, the observed decrease in sorption at higher pH is due to the formation of insoluble hydroxyl complexes of the metal ions [14].

In this study, at pH 1, the highest adsorption is shown for Cr$^{3+}$ in all three types of resins. For other metal ions, the
The graph shows much deviation for different types of resins as follows:

Dowex 50-X8: \( \text{Cr}^{3+} > \text{Cd}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \)

ACF: \( \text{Cr}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} \)

SCF: \( \text{Cr}^{3+} > \text{Cd}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \)

After a certain value of pH, \( \text{Cd}^{2+} \) shows higher adsorption in the Dowex resin. In the ACF resin, \( \text{Cd}^{2+} \) shows a low rate of ion exchange. After pH 3, ion-exchange capacity increases considerably in the Dowex rather than ACF and SCF resins (Table 1). Examination data presented in the above figures show that the amount of adsorbed metal ions increases with increasing concentration of metal ions in the solution to a maximum value and will remain constant while there is a new increase of metal concentration. At a low concentration of metal ions, the available number of metal ions in the solution is low relative to the arrangement sites on the sorbent. However, at higher concentrations, the available sorption sites remain the same as more metal ions are available for sorption, and subsequently sorption becomes almost constant thereafter.

4. Conclusion

Two formaldehyde-based resins derived from anthranilic acid-catechol and salicylic acid-catechol with formaldehyde were useful cation exchangers for divalent metal ions. The FTIR spectral analysis confirmed the assumed structure of these terpolymeric resins. Melting points of both resins were mostly high, and it indicates that the polymer resins under study are thermally stable up to a high temperature. Sorption studies of ACF suggest that the ion-exchange order of metal ions is dependent on the function of time. The synthesized resin can be used for the removal of heavy metals from aqueous media and industrial wastewater containing \( \text{Cr}^{3+}, \text{Mg}^{2+}, \text{Ca}^{2+}, \) and \( \text{Cd}^{2+} \). ACF is more suitable for removal of hardness from water when compared to SCF. SCF is a better chelating resin for removal of heavy metals. The recovery of the metals from industrial effluents gives an indication of the utilization potential of the synthesized resin for wastewater treatment.

Data Availability

Two formaldehyde-based terpolymeric resins (anthranilic acid-catechol-formaldehyde and salicylic acid-catechol-formaldehyde) have been synthesized by condensing anthranilic acid with catechol and salicylic acid with catechol, and their data are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References


