



RESEARCH ARTICLE

2-HAAT: A NEW NOVEL POLYMER POSSESSING EXCELLENT BIOLOGICAL ACTIVITIES AND ION EXCHANGE PROPERTIES

*Rahangdale, P. K.

Department of Chemistry, Bhawabhuti Mahavidyalaya, Amgaon-441902(India)

ARTICLE INFO

Article History:

Received 23rd March, 2016
Received in revised form
25th April, 2016
Accepted 08th May, 2016
Published online 15th June, 2016

Key words:

Condensation polymers,
Ion exchange resins,
Heavy metal toxicity,
Water treatment,
Biological activities.

ABSTRACT

The 2-HAAT novel polymer was synthesized through the acid catalysed condensation polymerization of 2-Hydroxy Acetophenone and Adipamide with Tioxane using proper molar ratio of the reacting monomers. The resulting polymer was characterized with Elemental Analysis, UV-Visible, FTIR and $^1\text{H-NMR}$ spectral data and SEM studies. The number average molecular weight of this novel polymer was determined with conductometric titration method in a non-aqueous medium. The chelating ion-exchange properties were also studied with the batch equilibrium method. The polymeric resin was proved to be selective chelating ion-exchanger for certain metals. The chelating ion-exchange properties of this polymer were studied for six metal ions viz. Cu^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} , Pb^{2+} and Fe^{3+} . The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed a higher selectivity for Pb^{2+} ions than for Cu^{2+} , Ni^{2+} , Cd^{2+} , Zn^{2+} and Fe^{3+} . The 2-HAAT polymer was tested for its inhibitory action against a few pathogenic bacteria and fungi. It has shown potent inhibitory action against bacteria, such as *Escherichia coli* and fungi viz. *Candida albicans*. Specific higher selectivity of this resinous novel polymer for Pb^{2+} proved its practical applicability for abatement of lead, a toxic heavy metal, from contaminated water and thus for water treatment.

Copyright©2016, Rahangdale. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Citation: Rahangdale, 2016. "2-HAAT: A new novel polymer possessing excellent biological activities and ion exchange properties", International Journal of Current Research, 8, (06), 32512-32518.

INTRODUCTION

De Geiso R.C., Donaruma L.G. and Tomic E. A. with their research group first suggested the use of copolymers and phenolic resins for ion-exchange purposes (Bhave, 1987; Saxena, 1991; Guivetchi, 1963 and Geil, 1981). Recently several copolymers have been reported (Rahangdale *et al.*, 2007; Gurnule *et al.*, 2003; Gurnule, 2003; Gurnule, 2002 and Gurnule, 2000) that possess properties useful for ion-exchange and biological activity purposes. Production and commercialization of ion exchange resins in a wide range of formulations with different characteristics have now a large practical applicability in various industrial processes, such as chemical industries, nuclear industries for treatment of liquid waste, pharmaceuticals, food industries etc (Alexandratos *et al.*, 1998; Singh *et al.*, 2009; Michael Pratik *et al.*, 2007; Rong-jun *et al.*, 2004 and Mane, 2009). The polymeric resins are used, both, in the field of ion exchange and heterogeneous catalysis for their versatile properties (Burkanudeen *et al.*, 2002; Karunakaran *et al.*, 2003 and Jadhao *et al.*, 2005). Organic ion exchange resin is the most important class of ion exchangers.

*Corresponding author: Rahangdale, P. K.

Department of Chemistry, Bhawabhuti Mahavidyalaya, Amgaon-441902, India

Several workers (Singru *et al.*, 2010) have investigated the role played by the polymer structure on ion exchange equilibrium and physical properties of the system. Riswan M. and Ahamed *et al.* (2010) reported the properties of ion exchangers containing chelate groups derived from anthranilic acid and formaldehyde. Ion exchange resins have been successfully employed for separation of components from many organic and inorganic mixtures. Polymeric resin derivatives possessing potent antibacterial/cytotoxic activities have been reported in the literature (Chaudhary, 2007). A series of cyano derivatives of N-alkyl and N-aryl piperazine were synthesized and their antimicrobial activities have been evaluated against Gram-positive and Gram-negative strains like *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *S. epidermidis*, *Escherichia coli* and antifungal activities against *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*. Parveen *et al* have reported biological evaluation of nitrogen containing aniline-formaldehyde resin as a potent antifungal and antibacterial agent (Parveen, 2008). Long chain aliphatic esters as well as organic and ferrocene containing Schiff's bases were synthesized and reported to have good antitumor, anticancer and antioxidant agents (Nawaz, 2009). Poly[(2-hydroxy-4-methoxybenzophenone) ethylene] resin and its polychelates with lanthanides(III) were screened for antibacterial activity and the metal chelated compounds have been found to possess

better activity compared to the ligands alone (Patel *et al.*, 2007). Keeping this view in mind it was planned to synthesize such a novel polymer, which bears combined properties of all of its monomers. The newly synthesized polymer was characterized by elemental analysis, UV-Visible, FT-IR, ^1H NMR spectral, SEM and number average molecular weight determination studies. One of the important applications of chelating and functional copolymers is their capability to remove/recover metal ions from waste solutions. Hence, the chelating ion-exchange properties of the 2-HAAT polymer resin have also been studied for specific metal ions along with its biological/antimicrobial properties for certain common microbes.

Experimental

Synthesis of 2-HAAT Novel polymer

The 2-HAAT novel polymer was synthesized by the condensation polymerization of 2-Hydroxy Acetophenone (0.2mol) and Adipamide (0.1mol) with Trioxane (0.1mol) in hydrochloric acid (0.1N) as a medium at 135 ± 1 °C in an oil bath for 5 hrs. The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove excess of 2-Hydroxy Acetophenone- Trioxane copolymer, which might be present along with the 2-HAAT novel polymer. The dried polymeric product was further purified by dissolving in 10% NaOH and regenerated in 1:1(v/v) HCl/water. The purified 2-HAAT polymer was finally ground well to pass through a 300 mesh size sieve and kept in a vacuum over silica gel. The yield of this copolymer resin was found to be 85.5% and the melting point is 550 ± 5 K. The sieved polymer was used for further studies.

Characterization of 2-HAAT novel polymer

The copolymer resin was subjected to micro analysis for C, H and N. The number average molecular weight \overline{M}_n was determined by conductometric titration in DMSO medium using ethanolic KOH as the titrant by using 25 mg of sample. A plot of the specific conductance against the milliequivalents of potassium hydroxide i.e. the base required for neutralization of 100 gm of copolymer was made. Inspection of such a plot revealed that there were many breaks in the plot. From this plot the first break and the last break were noted. The calculation of \overline{M}_n by this method was done using the following equation (Singru, 2010):

$$\overline{DP} = \frac{\text{(Total milliequivalents of base required for complete neutralization)}}{\text{(Milliequivalents of base required for smallest interval)}}$$

$$\overline{M}_n = \overline{DP} \times \text{molecular weight of the repeating unit}$$

Where, \overline{DP} \Rightarrow Degree of polymerization

And $\overline{M}_n \Rightarrow$ number average molecular weight

Spectral Analysis

Electronic (UV-visible) absorption spectra of the copolymer in DMSO/DMF was recorded with a double beam

spectrophotometer fitted with an automatic pen chart recorder on themosensitive paper in the range of 200 – 850 nm. Infrared spectra of 2-HAAT novel polymer was recorded in najol mull with Perkin-Elmer-Spectrum RX-I, FT-IR spectrophotometer in KBr pallets in the range of $4000 - 500 \text{ cm}^{-1}$ at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. ^1H NMR spectra was recorded with Bruker Adanve – II 400 NMR spectrophotometer using DMSO- d_6 as a solvent, at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh. The surface analysis was performed using scanning electron microscope at different magnifications. SEM has been scanned by JEOL JSM-6380A Analytical Scanning Electron Microscope at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.

Antimicrobial study

Antibacterial activity was tested by petri plate method involving the cultures of the selected organisms for 24hrs. Mueller Hinton agar no.2 (Hi Media, India) was used as the bacteriological medium. The test solutions of the synthesized polymer were prepared in sterile dimethyl sulphoxide solvent for the study. The synthesized novel polymer was tested at different concentrations ranging from 50 to 1000 ppm to find out the minimum concentration of the polymer required to inhibit the bacterial growth. Amoxicillin (100 $\mu\text{g}/\text{mL}$) was taken as the standard for antibacterial activity. The organisms were seeded into sterile nutrient agar medium by mixing 1 ml of inoculums with 20 mL of sterile melted nutrient agar kept at $48-50$ °C in a sterile petri dish. The medium was allowed to solidify first. Then the test solutions, the standard drugs as well as the blank were impregnated in Whatmann filter paper discs and placed on the solidified medium in the petri dish and left undisturbed for 2 hrs. at room temperature. The Petri dishes were then incubated at 37 °C for 24 h and the zone of inhibition for the test samples, standard and the control (DMSO) were measured. Antifungal activity was tested employing the similar technique involving the cultures of the selected organisms for 24 hrs.. Sterile yeast nitrogen base (HI Media) with 2% agar was inoculated by a rotating swab (soaked in standard inoculums suspension) over the surface of the media. Fluconazole (100 mg/ml) was taken as the standard for antifungal activity. The test solution impregnated discs were placed on the agar and incubated at 37°C for 18 h. The zone of inhibition was measured by measuring the minimum dimension of the zone of fungal growth around the filter paper disc.

RESULTS AND DISCUSSION

The resin sample was light yellow in color, insoluble in common organic solvents, but was soluble in dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, pyridine and concentrated H_2SO_4 . The newly synthesized novel polymer has melting point $550 \pm 5\text{K}$. Elemental analysis and molecular weight determination data have been presented in Table 1. Based on the analytical data, the empirical formula for repeating unit of the novel polymer was found to be $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_4$, which is in good agreement with the calculated values of C, H, N and O

Table 1. Elemental Analysis and molecular weight of polymers

Polymers	% of Carbon found (calculated)	% of Hydrogen found (calculated)	% of Nitrogen found (calculated)	% of Oxygen found	Empirical formula of repeat unit	Molecular weight of repeating unit	Number average molecular weight of the novel polymer
2-HAAT	63.14 (63.00)	6.62 (6.52)	9.20 (9.18)	21.03	C ₁₆ H ₂₀ N ₂ O ₄	304.34	7608.50

Characterization of copolymer resin

Conductometric titration graph has been presented in figure 6. The number average molecular weight (\bar{M}_n) could be obtained by multiplying the \bar{DP} by the formula weight of the repeating unit (Singru, 2008 and Silverstein *et al.*, 1987). The molecular weight for 2-HAAT polymer was found to be 7608.50.

Spectral Analysis

The UV-visible spectrum of 2-HAAT copolymer sample in pure DMF was recorded in the region 300–800 nm and the spectrum is presented in Fig 1. The 2-HAAT polymer sample displayed two characteristic broad bands at 265 nm and 315 nm (Singru *et al.*, 2010 and Singru *et al.*, 2008). These observed position for absorption bands indicate the presence of a carbonyl (>C=O) group having a carbon oxygen double bond which is in conjugation with the aromatic nucleus. The later band (less intense) can be accounted for $n \rightarrow \pi^*$ transition while the former band (more intense) may be due to $\pi \rightarrow \pi^*$ transition. The bathochromic shift (shift towards longer wavelength) from the basic value of >C=O group *viz.* 310 nm and 240 nm respectively, may be due to the combined effect of conjugation and phenolic hydroxyl group (auxochrome).

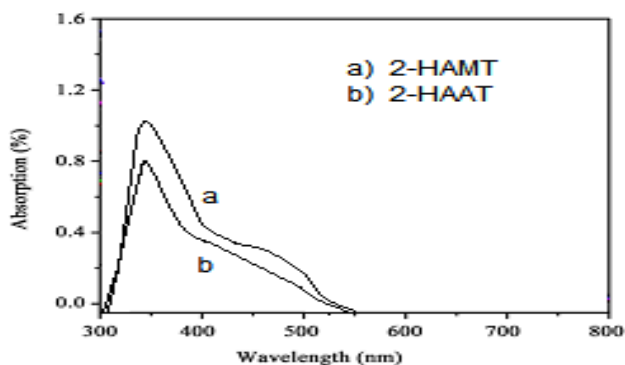


Figure 1. UV-Visible spectrum of 2-HAAT Novel Polymer

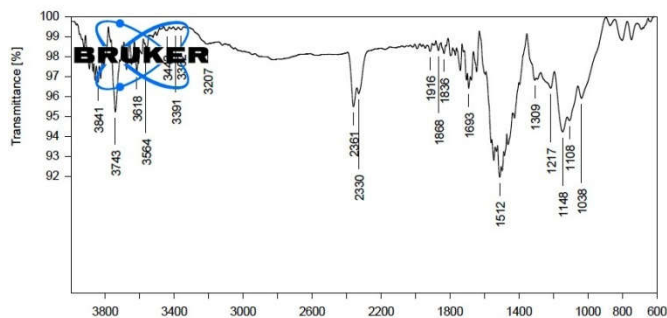
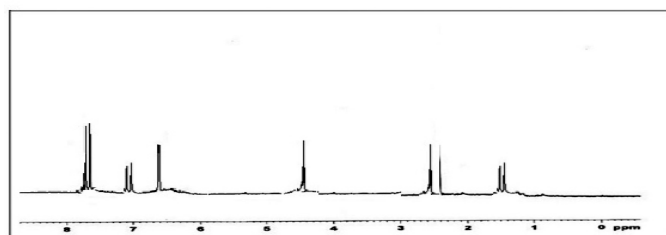


Figure 2. FTIR spectrum of 2-HAAT Novel Polymer

Figure 2 represents FTIR spectrum of the 2-HAAT Polymer. The incorporation of all monomer in the resultant Novel Polymer has been confirmed from this FTIR. The FTIR spectrum of the 2-HAAT Polymer provides qualitative information about the composition of the polymer. A band at 1495-1520 cm^{-1} is due to aromatic ring stretching. Appearance of band at 3382-3618 cm^{-1} and 1108-1038 cm^{-1} is due to aromatic C-H stretching and aromatic C-H bending (in the plane) respectively. Appearance of band at 850-650 cm^{-1} may be because of asymmetric aromatic C-H bending (out of plane). Other peaks in the polymer spectrum are found to be shifted in comparison with the corresponding peaks of the homopolymers of the monomers as per the standard reference (Silverstein *et al.*, 1987; Kemp *et al.*, 1975 and Patle *et al.*, 2010). This shows that the polymer formed is a pure polymer and not a mixture of homopolymers.

Figure 3. ¹H NMR spectrum of 2-HAAT Polymer

¹H NMR spectrum of 2-HAAT polymer has been presented in Figure 3. ¹H NMR data of 2-HAAT novel polymer shows a weak multiplicity signals (unsymmetrical pattern) in the region 7.6 to 7.7 (δ) ppm may be due to the aromatic protons. The weak multiplet signals appearing at 5.2 – 5.2 (δ) ppm may due to the amido –CH₂ -NH-CO linkage. A signal appeared in the region 4.9 – 4.9 (δ) ppm may be due to proton of methylenic bridges (Ar – CH₂ – N) of polymer chain. A weak signal appeared in the region of 2.1 - 2.6(δ) ppm may be due to the Ar-CO-CH₃ group. The signal in the range of 3.4 – 3.6 (δ) ppm is attributed to protons of phenolic –OH (Kalsi, 1995). Number of sets of equivalent protons and position of the signals are matching with the most probable (proposed) structure, which is again an indicative of successful synthesis of the new polymer.

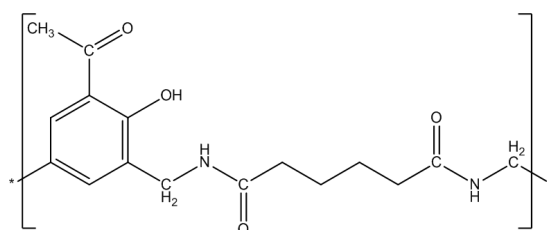


Figure 4. Structure of 2-HAAT Polymer

On the basis of physicochemical and spectral evidences the most probable structure has been proposed for 2-HAAT novel polymer which is presented in Figure 4.

Scanning Electron Micrograph

Figure 5 represents SEM image of 2-HAAT polymer. The surface appears to be highly porous. The SEM micrograph indicates that the pores were made up of cylinder like tubes, which would easily capture and retain the metal ions from aqueous solution. The pore size is found to be approximately $3.82\mu\text{m}$ (Kaur *et al.*, 2009 and Suzuki, *et al.*, 2002). Surface analysis has found great use in understanding the surface features of the materials. The morphology of the reported polymer sample was investigated by scanning electron micrograph. It gives the information of surface topology and defect in the structure, if any. The morphology of novel resinous polymer has been assigned from Spherule and Fringed model. The spherules are complex polycrystalline formation having as good as rough surface. This indicates the crystalline nature of p-HAAT novel polymer sample. Due to the deep pits (Kaur *et al.*, 2009 and Suzuki, *et al.*, 2002) the resinous polymer exhibits higher exchange capacity for Pb^{2+} ions (as well as other many metal ions). This could be the reason of bigger nitrated Pd^{2+} ions, which can easily penetrate in to the deep pits.

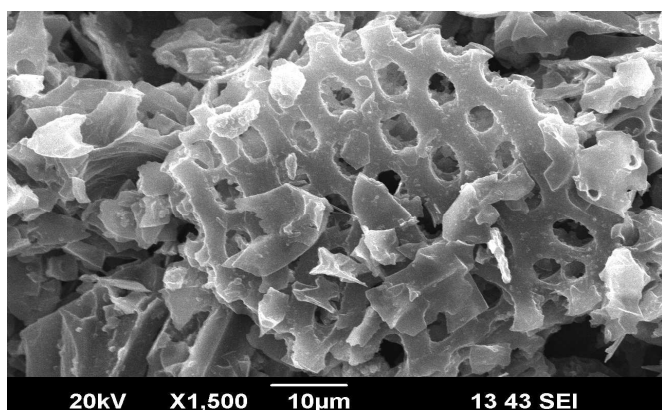


Fig. 5. SEM Micrograph of p-HAAT novel polymer at 1500x magnification

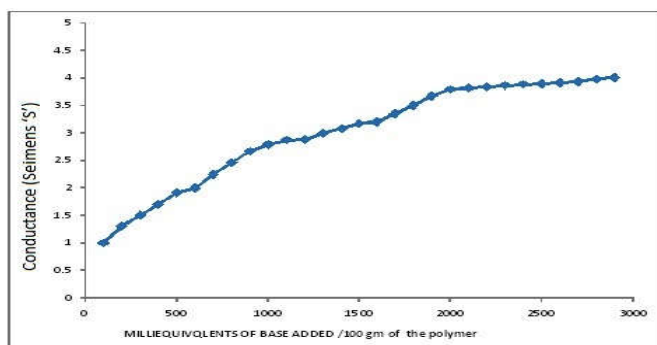


Fig 6 Conductometric titration curve of 2-HAAT polymer

Antimicrobial testing

The results of microbial screening of the 2-HAAT novel polymer are presented in Figure 7 and Table 2 for antibacterial

and antifungal studies. In this study, the antimicrobial activity of 2-HAAT novel polymer using petri plate method has been evaluated. In this analysis, the novel polymer under present investigation displayed antimicrobial activity against a few pathogenic microorganisms. The results have been presented in Table 2. From the results it can be concluded that, the novel polymer under present study has shown a good antimicrobial activity against *E. coli* and *C. albicans*. The petri plates were marked as A and B where A contains culture supernatant and (B) Polymer control respectively. An admirable result was obtained for 2-HAAT novel polymers against *Escherichia coli* bacterium which is markedly higher than the standard. *E. coli*, a gram negative rod-shaped bacterium, which affects the urinary tracts in humans. The antifungal activities of the 2-HAAT novel polymers also provide appealing results against the chosen fungal strains. *Candida albicans* is a diploid fungus and a causal agent of opportunistic oral and genital infections in humans and also emerged as an important cause of morbidity and mortality in immuno compromised patients. The antimicrobial activity of the novel polymers may be due to the presence of $-\text{NH}_2$ and $-\text{OH}$ groups. It is perceived that the factors, such as solubility, conductivity, dipole moment and cell permeability may also contribute to the increased antimicrobial activity against the chosen microbes (Nawaz, 2009; Patel *et al.*, 2007).

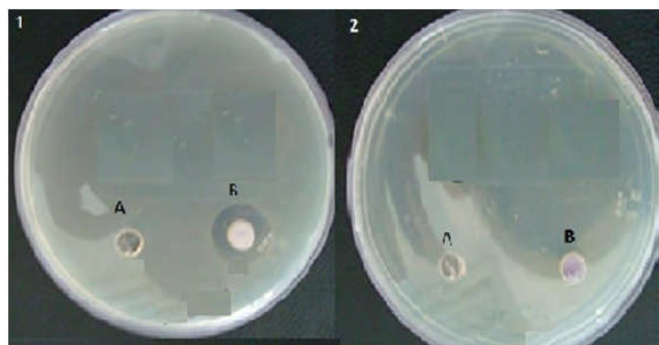


Figure 7. Antimicrobial activity of 2-HAAT Polymer (Plate 1 for *Escherichia coli* & plate 2 for *Candida albicans*). Each plate shows (A) culture supernatant and (B) Polymer control respectively

Table 2. Diameter zone of inhibition by 2-HAAT novel polymer against a few microorganisms

Polymer	Microorganism	Zone of inhibition (mm in diameter)
2-HAAT	<i>Escherichia coli</i>	15.34
	<i>Candida albicans</i>	10.87

Ion-exchange properties

With a view to ascertain the influence of various electrolytes on the selectivity of metal ions, the rate of metal uptake and the distribution ratio of metal ions between the polymer and solution containing the metal ions, ion-exchange properties of 2-HAAT novel polymer have been studied, employing batch equilibrium method (Vogal, 2009 and Kunin, 1971). The 2-HAAT polymeric resin shows that the group $-\text{OH}$ and $-\text{NH}$ contain lone pair of electrons, which can be donated to the metal ion during complex formation. Hence it shows chelating

behavior. When polymer is suspended in metal ion solution, the chelating tendency of copolymer forms the cyclic complex with the metal ions, which absorbs the metal ion from solution to surface of polymer. This mechanism of adsorption of metal ion by polymer ligands is known as metal uptake of polymer. Due to metal uptake concentration of metal ion in solution decreases, this can be determined by titration with standard EDTA solution or using Atomic Absorption Spectrophotometer (AAS). The metal uptake capacity of polymer is different for different metal ion, is also known as selectivity of polymer towards the uptake of metal ion. The metal uptake of polymer depends on three variables, concentration of electrolyte solution, shaking time and pH of the solution. The chelating behavior of 2-HAAT polymer was studied with these three variables by keeping two variable constant at each time. Batch equilibrium technique developed by Gregor *et al.* and DeGeiso *et al.* was used to study of ion exchange properties of 2-HAAT copolymer resin. The results of the batch equilibrium study carried out with the copolymer resin 2-HAAT have been presented in this article. Six metal ions Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} in the form of aqueous metal nitrate solution were used. The ion exchange study was carried out using three experimental variables: (a) electrolyte and its ionic strength (b) shaking time and (c) pH of the aqueous medium. Among three variables, two were kept constant and only one was varied at a time to evaluate its effect on metal uptake capacity of the polymer (Kunin, 1971; Kunin, 1962 and Helfferich, 1998).

Effect of electrolytes and their concentration on the metal ion uptake capacity

The effect of NO_3^- , Cl^- , SO_4^{2-} and ClO_4^- at various concentrations on the equilibrium of metal resin interaction of constant pH. Different metal ions have different pH in solution, has been presented which shows that the amount of metal ions taken up by a given amount of copolymer depends on the nature of concentration of the electrolyte present in the solution. In the presence of nitrates, perchlorate and chloride ions the uptake of Fe^{3+} , Cu^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions increasing with increasing concentration of electrolytes; whereas in the presence of sulphate ions, the amount of above maintained ions taken up by the copolymer resin decreases with increasing concentration of the electrolyte (Gruyter Walter de, 1992). Above NO_3^- , Cl^- , and ClO_4^- ions form weak complex with the above metal ions, while SO_4^{2-} form stronger complex thus the equilibrium is affected. This may be explained on the basis of the stability constants of the complexes with those metal ions and nature of ligands.

Rate of metal ion uptake as a function of time

The rate of metal adsorption was determined to find out the shortest period of time for which equilibrium could be carried out while operating as close to equilibrium condition as possible. During rate of metal ion determination, the concentration of metal ion and electrolyte solution and pH of the solution was kept constant. As shaking time increases the polymer gets more time for adsorption, hence uptake of metal ions increases. The rate refers to the change in the concentration of the metal ions in the aqueous solution which

is in contact with the given copolymer. It was noticed that the time taken for the uptake of the different metal ions at a given stage depends on the nature of metal ions under given conditions. It is found that Pb^{2+} ions required about 3 hrs for the establishment of the equilibrium, whereas Cu^{2+} , Zn^{2+} and ions required about 6 hrs. Thus the rate of metal ions uptake follows the order $\text{Pb}^{2+} \gg \text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+}$ for the 2-HAAT copolymer (Gruyter Walter de, 1992; and Harland, 1994). Thus the polymeric resin under study shows very high selectivity for Pb^{2+} .

Distribution ratios of metal ions at different pH

The distribution of metal ion depends upon pH of the solution. By increasing pH, the H^+ ion concentration in the solution decrease and only metal ion in the solution available for adsorption which increase uptake of metal ions. The data on the distribution ratio as a function of pH indicate that the relative amount of metal ions taken up by the resinous polymers increase with increasing pH of the medium (Patle, 2010). The magnitude of increase, however, is different for different metal cations. The study was carried out from 2.5 up to pH 6.5 to prevent hydrolysis of metal ions at higher pH. The selectivity of Pb^{2+} ion is more for the 2-HAAT copolymer resin as compare to the any other metal ions under study. The order of distribution ratio of metal ions measured in the range, 1.5 to 6.5 is found to be $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Fe}^{3+} > \text{Zn}^{2+}$ (Gruyter Walter de, 1992). Thus the results of such type of study are helpful in selecting the optimum pH for a selective uptake of a particular metal cation from a mixture of different metal ions [32, 36]. For example, the result suggests the optimum pH 2.5 for the separation of Pb^{2+} and Zn^{2+} with distribution ratio 'D' is 785.8 and 88.4 respectively using the 2-HAAT copolymer resin as ion exchange. Similarly for the separation of Pb^{2+} at the optimum pH is 2.5 with distribution ratio is 348.8 for 2-HAAT copolymer. The lowering in the distribution ratios of Pb^{2+} was found to be small hence, efficient separation could be achieved. Thus the separation of $\text{Pb}(\text{II})$ from other metal having combination (1) Pb^{2+} and Cu^{2+} , (2) Pb^{2+} and Zn^{2+} , (3) Fe^{3+} and Zn^{2+} , (4) Fe^{3+} and Pb^{2+} etc. can be effectively separated out.

Conclusions

- Synthesis of a new novel polymer i.e. 2-HAAT using starting materials like 2-Hydroxy Acetophenone, Adipamide and Trioxane is successful.
- The characterization and structure elucidation on the basis of various physicochemical and spectral methods for newly synthesized novel polymer is also successful.
- The antimicrobial (biological) activities of the new novel polymer under investigation have been evaluated for microorganisms like *Escherichia coli* and *Candida albicans*. The polymer has been found to possess good antimicrobial activities for the above mentioned microbes.
- Ion exchange property studies reveal that the novel polymer can act as an effective ion exchanger for various trivalent and divalent metal ions such as Fe^{3+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} and Pb^{2+} . The 2-HAAT polymer has immense applications as an ion exchange resin in waste water treatment, metal recovery and for the identification of specific metal ions. The copolymer showed a higher

selectivity for Pb^{2+} ions than for Cu^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+} and Zn^{2+} ions.

- Very high selectivity of 2-HAAT toward Pb^{2+} proves the practical applicability of this novel polymer in water treatment for removal of toxic metals like lead from contaminated water.

Prospective of future work

The studies can be extended to evaluate antimicrobial activities of this new novel polymer against a large variety of other microorganisms. Moreover these new novel polymers can be studied in light of their practical applicability as semi-conductors, ion-exchangers and adsorbents for removal of many other toxic pollutants from contaminated water. Surface modification of this newly obtained novel polymer can be done employing molecular absorption deposition of nanostructured photocatalytic materials like AgI-ZnO. The advanced photocatalytic functional materials obtained this way can be successfully used for photodegradation of dye pollutant and thus they can have potential applications in waste water treatment.

Acknowledgements

The author is highly thankful to Dr. S. M. Bhuskute, Principal, Bhawabhuti Mahavidyalaya Amgaon for his kind cooperation during forwarding of the proposal of MRP to UGC and his timely help during the course of this investigation after sanction period of the project. The investigator is also thankful to UGC (WRO) for sanctioning the project and providing financial assistance. The investigator is highly grateful to the Dr. D. K. Burghate, Principal, Shri Shivaji Science College Nagpur for allowing the use of Chemistry Research Laboratory of his college during the course of this investigation.

REFERENCES

- Ahamed, M. R., Azarudeen, R., Karunakaran, M., Karikalan, T., Manikandan, R., Burkanudeen, A.; Cation Exchange Properties of a Terpolymer: Synthesis and Characterization 2010. *J of Chem. and Envir. Engg.*, 1, 7-12.
- Alexandratos, S.D., Shelley, C.A., Horwitz, E.P., and Chiarizia R. ; A mechanism for enhancing ionic accessibility into selective ion exchange resins, 1998. *Solv. Extr. Ion Exch.*, 16(4) 951–966.
- Bhave, N. S., Iyer V. N. Thermal degradation of some coordination polymers, 1987. *J. Therm. Anal.*, 32, 1369
- Burkanudeen, A., and Karunakaran, M.; Chelation ion-exchange properties of orthonitrophenol - Thiourea-para formaldehyde terpolymer, 2002. *Orient. J. Chem.*, 18 65–68.
- Chaudhary, P., Nimesh, S., Yadav, V., Verma, A.K. and Kumar, R.; Synthesis, characterization and in vitro biological studies of novel cyano derivatives of N-alkyl and N-aryl piperazine, 2007. *European Journal of Medicinal Chemistry*, 42, p. 471.
- Geil, P. H.; The morphology of crystalline polymers 1981. *J. Chem. Edn.*, 58.
- Gruyter Walter de, 1992. Ion Exchangers (K. Dorfner, ed.), Berlin, 1992.
- Gurnule W. B., Rahangadale P. K., Paliwal L.J. and Kharat R.B. 2003; Chelation Ion-Exchange Properties of a Copolymer Derived from 2-Hydroxyacetophenone, Oxamide and Formaldehyde Synth. *React. Inorg. Met. Org. Chem.*, 33(7) 1187-1205.
- Gurnule, W. B. 2003. Rahangadale P. K., Paliwal L.J. and Kharat R.B; Synthesis, characterization and ion-exchange properties of 4-hydroxyacetophenone, biuret and formaldehyde terpolymer resins.; *React. and Funct. Polym.*, 55 255-265.
- Gurnule, W. B., Rahangadale, P.K., Paliwal, L.J. and Kharat R.B.; Chelation ion- exchange properties of copolymer resins derived from 4-hydroxyacetophenone, oxamide and formaldehyde 2003. *J. Applied Polym. Science*, 89(3), 886-889.
- Gurnule, W.B., Juneja, H.G. and Paliwal, L.J.; Ion-exchange properties of a salicylic acid–melamine–formaldehyde terpolymer resin, 2002. *React. Funct. Polym.*, 50, 95-100.
- Gurnule, W.B., Juneja, H.G. and Paliwal, L.J. Ion-exchang; properties of 8-hydroxyquinoline-biuret-formaldehyde tercopolymers, 2000. *Indian J. Chem.*, 39(A) 1110
- Gurnule, W.B., Rahangadale, P.K., Paliwal, L.J. and Kharat R.B.; Synthesis and characterization of copolymer derived from 2 –hydroxyacetophenone, oxamide and formaldehyde, 2002. *Prog. Cryst Grow. and Charact., of Mat.*, 45, 133-138.
- Harland, C. E. 1994. Ion exchange: Theory and Practice, The Royal Society of Chemistry, Cambridge.
- Helfferich, F, Ion Exchange, McGraw-Hill; Non-linear waves in chromatography II. Wave interference and coherence in multicomponent systems, 1998. New York, 75- 233.
- Jadhao M.M., Paliwal, L.J., and Bhave, N.S.; Resin I: Synthesis and characterization of 2,2'-dihydroxybiphenyl–urea–formaldehyde terpolymers, 2005. *J. Appl. Polym. Sci.*, 96 1605–1610.
- Kalsi, P.S. 1995. Spectroscopy of Organic Compounds, 2nd ed., New Age International, New Delhi.
- Karunakaran, M. and Burkanudeen, A.; Synthesis, Characterization, Metal Ion Binding Capacities and Applications of a Terpolymer Resin of Anthranilic acid/Salicylic acid/Formaldehyde 2003. *Orient. J. Chem.*, 2003, 18, 225–228.
- Kaur, H. 2009. Strumental methods of chemical analysis, Arihant Electric Press: Meerut.
- Kemp, W. 1975. Organic Spectroscopy; Macmillan: Hong Kong. 89.
- Kunin, R. 1958. Ion Exchange Resins, 2nd ed., Wiley, New York, 1962, 325, 337, 345.
- Kunin, R., R. Kreiger, E. 1971. Elements of Ion Exchange, (Ed.), Huntington, Huntington, New York, 163.
- Mane, V.D. Wahane, N.J. and Gurnule, W.B.; Copolymer resin. VII. 8-hydroxyquinoline-5-sulfonic acid–thiourea–formaldehyde copolymer resins and their ion-exchange properties 2009. *J. Appl. Polym. Sci.*, 111, 3039–3049.
- Michael Pratik, E.P., Barbe, J.M., Juneja, H.D., and Paliwal, L.J. ; Synthesis, characterization and thermal degradation of 8-hydroxyquinoline –guanidine –formaldehyde terpolymer, 2007. *Eur. Polym. J.*, 43 4995–5000.
- Nawaz, H. Nawaz, Z. Akhter, S. Yameen, H.M. Siddiqi, B. Mirza and A. Rifat; Nawaz, H. Nawaz, Z. Akhter, S.

- Yameen, H.M. Siddiqi, B. Mirza and A. Rifat, 2009. *Journal of Organo-metallic Chemistry*, 604, p. 2198.
- Parveen, S., Ahamad, T., Malik, A. and Nishat, N. Antimicrobial activity of aniline-formaldehyde resin modified by adding piperazine moiety and its metal polychelates 2008. *Polymers for Advanced Technologies*, 19, p. 1779.
- Patel, M.M., Kapadia, M.M., Patel, G.P. and Joshi, J.D.; Synthesis, characterization, ion-exchange and antimicrobial study of poly[(2-hydroxy-4-methoxy benzophenone ethylene) resin and its polychelates with lanthanides(III) 2007. *Reactive and Functional Polymers*, 67, p. 746.
- Patle, D. B., Gurnule, W. B. ; Metal ion binding properties of a copolymer resin: synthesis, characterization, and its applications, 2010. *Polymer Bulletin*, 66, 803-820.
- Rahangdale, S. S., Zade, A. B. and Gurnule, W. B.; Chelation ion-exchange properties of 2-hydroxyacetophenone-oxamide-formaldehyde terpolymer resin 2007. *Ultra Science*, 19(2) 213-218
- Rong-jun, Q., J. Chun-nuan, S. Yan-zhi, L. Zhong-fang, C.Guo- xiang, and Ren-feng, S.; Thermal Degradation Studies of Terpolymer Derived from 2-Aminothiophenol, Hexamethylenediamine, and Formaldehyde, 2004. *Chinese J. Polym. Sci.*, 2004, 22(5), 469-475.
- Saxena, N, Munshi, K.N.; The antimicrobial activities of the new ... Anal. 1991. *J. Therm. Anal.*, 37, 2250.
- Silverstein, R. M., Bassler, G. C. 1987. *Spectrometric Identification of Organic Compounds*, 2nd ed.; Wiley: New York., 56.
- Singh, A., and Saraf, S.K. ; Synthesis, Characterization and Ion-Exchanging Properties of a Novel Ion-Exchange Resin, Part II 2009. *Int. J. Polym. Mater.*, 58(10) 499-508.
- Singru, R.N. and Gurnule, W.B. Chelating Ion-exchange Properties of Copolymer Resins Derived from p-Cresol, Oxamide and Formaldehyde 2010. *Iran. Polym. J.*, 9(3), 169-183.
- Singru, R.N., Gurnule, W. B., Khati, V. A., Zade, A. B. and Dontulwar, J. R.; Eco-friendly application of p-cresol-melamine-formaldehyde polymer resin as an ion-exchanger and its electrical and thermal study 2010. *Desalination*, 263, (3). 200 - 210.
- Singru, R.N., Zade, A. B., Gurnule, W.B. 2008. Synthesis, characterization, and thermal degradation studies of copolymer resin derived from p-cresol, melamine, and formaldehyde, *J. Appl Polym Sci.*, 109, 859-868.
- Suzuki, E. 2002. High Resolution Scanning Electron Microscopy of Immunogold Labeled cells by the use of thin plasma coating osmium, *J Microscopy*, 153, 208.
- Vogel, S., *Textbook of Quantitative Chemical Analysis*, Sixth Edition. 2009.
