



Development and Application of Newly Synthesized Mango Seed Starch 6-Amino Hexanoic acid Resin for Elimination of Toxic Heavy Metal Ions from Industrial Effluents

**GANESH KUMAR CHOUDHARY^{1*}, ANJU², CHANDRA PRAKASH³,
SARITA KUMARI⁴, MUKESH CHOUDHARY⁵ and VIMLA CHOWDHARY⁶**

^{1,2,3,4,5,6}Department of Chemistry, Jai Narain Vyas University, Jodhpur, Rajasthan, 342001, India.

*Corresponding author E-mail: ganeshkumarchoudhary12@gmail.com,
anjuchoudharyjnvujodhpur@gmail.com

<http://dx.doi.org/10.13005/ojc/390423>

(Received: July 14, 2023; Accepted: August 16, 2023)

ABSTRACT

Newly synthesized resins are used for sustainable development with an eco-friendly nature. Extensive study on productivity and application aspects of these resin has attracted the attention of the scientific community. With this aim, the present work reports the newly synthesized mango seeds-based resin. The developed resins are useful for elimination of toxic heavy metal ions. A newly synthesized mango seed starch 6-amino hexanoic acid (MSSAHA) resin has been studied and found to have potential for elimination of industrial effluents. The influence of pH on adsorption has been studied. The newly synthesized MSSAHA resin was further diagnosed by SEM, TGA and FTIR spectral analysis. Metal ion distribution coefficient (K_d values at pH 7) for Fe^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} are 86.66, 60.95, 69.42, 49.44 and 45.65, respectively. Metal ions removal from waste water for Fe^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} and Pb^{2+} are 89.65%, 85.90%, 87.40%, 83.17% and 82.03%, respectively. These heavy metal ions have selectively separated by MSSAHA resin. The resin has been also examined for removal of Fe^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} in different solutions.

Keywords: Starch, Effluent, Elimination, Mango seed starch-6-amino hexanoic acid, Metal ions.

INTRODUCTION

Untreated industrial waste water contains toxic metal ions such as mercury, lead, chromium, cadmium, and arsenic that have been linked to either acute or chronic toxicities.¹⁻³ Exploring novel active adsorbents as effective removal agents for hazardous metal ions that pose health risks to people and other organisms is urgently necessary. The numbers classical methods have been so far used to remove

toxic heavy metals as solvent extraction⁴, precipitation and coprecipitation⁵, electrochemical reduction⁶, biosorption⁷, pre-concentration⁸ for the efficiency of the scientific method, researchers are very interested in heavy metal removal using various adsorbent resins.

Adsorbent that has been reported for their effective removal such as chitin⁹⁻¹⁰, chitosan¹¹⁻¹², cellulose¹³⁻¹⁵, commercially activated carbon¹⁶⁻¹⁷ and guar gum¹⁸⁻²¹. The starch-based resin has been



attracted by number of researchers for absorbance toxic metal ions from industrial waste, as starch is eco-friendly as well as cost effective²². Mango is one of the common fruits in Asia, Central and South America and Africa particularly. Average of 15 million t (MT) Mango in a year is produced in India²³. Mango seed is reported as sustainable and potential source of starch²⁴. The outcomes of study done by paying attention to enhance the results by selecting the particular compounds in innovation for noble work for their commercial viability²⁵. Heavy metals present in water above the acceptable limit are severe hazards to livings and they are non-biodegradable in different environmental conditions. Therefore, it is urgent attention for adequate treatment and regulations²⁶. Waste water pollution from hazardous heavy metals is regarded as effect on population growth²⁷. The study explores synthesis and characterisation of cost-effective, co-friendly resin of mango seed starch-6-aminohexanoic acid and its adsorbent potency to extract toxic heavy metal ions from the industrial contaminants of Kusal Metals Industry present in Jodhpur, India, by batch method. It has also been investigated how pH affects the ability of hazardous heavy metal ions to bind to surfaces.

MATERIALS AND METHODS

Materials

The chemicals used in the synthesis of resin are tabulated in Table 1.

Table 1: Materials used for development and application of newly synthesized MSSAHA Resin

Chemicals	Specification
Dioxane (AR)	Loba Chemie Pvt. Ltd. Mumbai, India
Epichlorohydrin (AR)	Molychem, Mumbai, India
6-aminohexanoic acid (AR)	Sigma-Aldrich Chemie GmbH, Germany
Sodium Hydroxide (AR)	S.D. Fine Chem. Pvt. Ltd. Boisar
Methanol (AR)	Loba Chemie Pvt. Ltd. Mumbai, India
Hydrochloric Acid	Ases chemical works, Jodhpur, India
Mango seed Powder	Extracted from mango seed kernel
Pumpkin Powder	Extracted from pumpkin pulp
Guargum Powder	Sarabhai M. Chemicals, Baroda, India

Methods for MSSAHA resin preparation

Mango seed powder was extracted from mango seeds (Fig. 1a, and b). The dioxane, Hydrochloric acid and 6-aminohexanoic acid used were of high purity. The reported MSSAHA resin (Fig. 1c) was synthesized by method of Singh

et al.,²⁸ A round-bottom flask was taken and it was filled with mango seed powder and a 0.2 mol slurry was prepared by dissolving in dioxane. 8.5 pH of solution was maintained by addition of 15 mL of 40% sodium hydroxide (w/v) in above obtain slurry. The solution was shacked at 60°C. 0.1 mol epoxy chloropropane was then added with continue shacking in solution. At 60°C temperature shacking was continued for 5 hours. Epoxypropyl ether of mango starch so obtained was then filtered under vacuum, methanol was used for washing and it was dried on filter paper. This epoxypropyl ether Mango seed starch was treated with 0.1 mol 6-aminohexanoic acid and the mixture was Shaked at the temperature of 60°C about 5 hours. This content was left for overnight. Next day it was filtered and methanol (90%) consisting 5 drops hydrochloric acid was employed for washing to remove inorganic contaminants. Pure methanol was further used for washing MSSAHA resin was obtained as yellowish-brown powder that had yield of 208.7 gram.



Fig. 1a. Mango seeds for development of newly synthesized MSSAHA resin



Fig. 1b. Mango seeds for development of newly synthesized MSSAHA resin



Fig. 1c. Newly synthesized MSSAHA resin

RESULTS AND DISCUSSION

Batch method

Batch method was employed for determination of distribution coefficients (K_d) and for the analysis of metal ions percentage removal by resin. The pH of solution was adjusted using two buffers of KCl-HCl buffer and acetate buffer. A sample solution (100 mL) was taken to 250 mL Erlenmeyer flask and pH was adjusted. After adjustment of pH of MSSAHA resin (100 mg) was taken in to the solution, this mixture was continuously shaken at 25°C temperature for about 2 h and equilibrium was attained. Whatman filter paper no. 40 was used for filtration. The residue so obtained after filtration was then equilibrated with 4N HCl. This content was again filtered using whatman filter paper 42. Perkin-Elmer model (2380) AAS was employed for analysis of the contaminating metal ions present in the filtrate obtain as well as adsorbed on the residue. The calibration curves for Fe^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} ions were plotted. The calibration curves were obtained Filtrate to determine the concentrations of these metal ions present in the filtrate. K_d (distribution coefficient) values and percentage adsorption of Fe^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} on MSSAHA resin were calculated.

$$K_d = \frac{\text{Amount of metal ion in resin/Dry resin weight (g)}}{\text{Amount of metal ion in solution/Solution volume (ml)}}$$

Thermo gravimetric analysis (TGA)

TGA was performed for newly synthesized mango seed starch 6-amino hexanoic acid (MSSAHA) resin for elimination of toxic heavy metal ions from Industrial Effluents. Vacuum desiccator was used for drying and powdering MSSAHA resin. It was packed for analysis at fix heating rate of 20°C per minute in atmosphere of air. The thermo gram of MSSAHA resin was studied for thermal decomposition up to 495°C under inert conditions. Thermo gravimetric analyser TGA Model Q 500 V 6.7 Build 203 was employed to determine the thermal behaviour of synthesized resin. Elements C, H, and O were determined in synthesized resin by Model Carlo Erba 1160 elemental analyser. Thermogram first breaks at 50°C, where there is a 10% weight loss that is primarily caused by water desorption. At 180°C, there is a second breakdown and a 60% weight loss. At the third breakdown, which occurs at 350°C, weaker bonds break down, causing weight loss of 10%. The thermogram of the MSSAHA resin is shown in Figure 2.

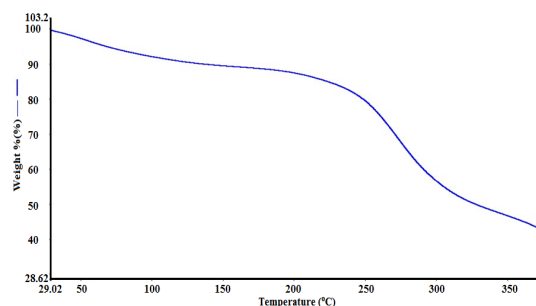


Fig. 2. TGA of the Mango Seed Starch-6-Amino hexanoic acid resin

Scanning Electron Microscopy (SEM)

SEM was performed for newly synthesized mango seed starch 6-amino hexanoic acid (MSSAHA) resin for elimination of toxic heavy metal ions from Industrial Effluents. Porous and rough surface of resin was clearly revealed by the micrographs. SEM was carried out by Zeiss instrument. Uneven and porous surface of resin is clearly revealed by SEM results. Synthesized resin has more rough structure as compared to mango seed powder. SEM observations are in good agreement with adsorption observations of metal ions present in effluent. Micrographs so obtained of MSSAHA resin are represented in Figure 3.

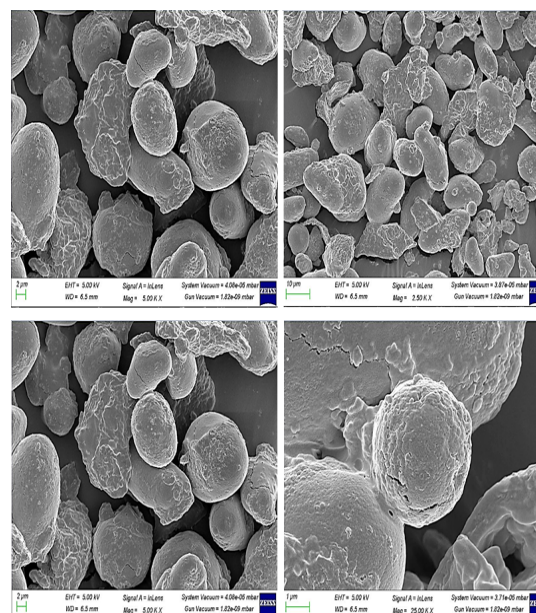


Fig. 3. SEM analysis of the mango seed starch-6-amino hexanoic acid resin

Infrared spectroscopy (FTIR)

FTIR spectral study was also performed for newly synthesized mango seed starch 6-amino

hexanoic acid (MSSAHA) resin for elimination of toxic heavy metal ions from Industrial Effluents. Characterisation of MSSAHA resin was carried out by FTIR instrument Perkin Elmer spectrum version 10. 4. 00., and KBr pellets were used for sample preparation. Atomic absorption spectrometer Perkin-Elmer Model 2380 was employed to concentration analysis of Fe²⁺, Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺ ions in reference and industrial waste water. IR spectral study was done with Perkin Elmer spectrum version 10. 4. 00 instrument using KBr pellets. The MSSAHA resin's FTIR spectrum exhibits a wide band due to stretching of -OH causing peak between 3600 and 3200 cm⁻¹. Stretching vibrations of C-H are responsible for the peak at 2923.14 cm⁻¹, N-H bending vibrations are found responsible for the peak at 1563.31 cm⁻¹, and C-H bending vibrations are responsible for the peak at 1357.31 cm⁻¹. C-O stretching vibration is shown by a prominent peak at 1002.70 cm⁻¹. FTIR of the MSSAHA resin is shown in Figure 4.

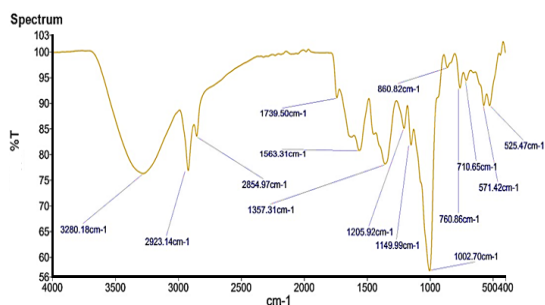


Fig. 4. FTIR of the mango seed starch-6-aminohexanoic acid resin

Distribution coefficient (Kd)

The adsorption potency of MSSAHA resin for Fe²⁺, Cd²⁺, Pb²⁺, Cu²⁺, Zn²⁺ ions from standard

solution and industrial effluent of Kushal Metals Industry, Jodhpur was investigated under different conditions of pH. Characteristics features of effluent are represented by Table 1. By using the batch approach, K_d (distribution coefficient) values of metal ions has been calculated. Table 2 provides the K_d (distribution coefficients) values of metal ions from the effluent of the Kushal Metals Industry in Jodhpur. Table 3 displays the percentage of metal ion's removal from effluents by the MSSAHA resin. Fig. 5, a graph between K_d and pH, illustrates the impact of pH on the of metal ions adsorption. The pH-dependent percentage of metal ion removal from effluents is shown in Figure 6.

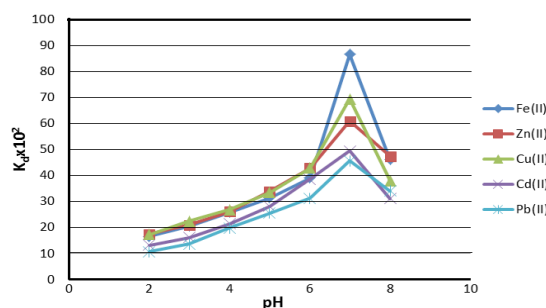


Fig. 5. Graph between K_d and pH

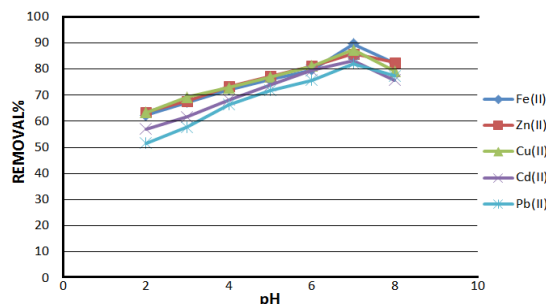


Fig. 6. Graph of percentage of removed metal ions with pH

Table 1: The significant characteristics of industrial waste water of Kushal Metals Industry, Jodhpur
 Visibility: Turbid, solution Colour: Greenish blue, Odour: Unpleasant, pH: 6.1, Total hardness: 959

Metal ions	Ca ²⁺	Mg ²⁺	Fe ²⁺	Zn ²⁺	Cu ²⁺	Cd ²⁺	Pb ²⁺
Concentration (in mg/L ⁻¹)	102.16	41.34	3.48	6.67	4.13	1.07	1.28

Table 2: Metal ion distribution coefficient (K_d) from Kushal Metals Industry wastewater, Jodhpur,

pH	Metal ion distribution coefficient (K _d) K _d × 10 ²				
	Fe ²⁺	Zn ²⁺	Cu ²⁺	Cd ²⁺	Pb ²⁺
2	16.56	17.44	17.35	13.26	10.64
3	20.52	21.02	22.51	16.09	13.70
4	25.87	26.14	26.87	21.47	19.76
5	31.42	33.88	33.47	28.21	25.55
6	39.01	42.93	42.94	38.63	31.29
7	86.66	60.95	69.42	49.44	45.65
8	46.12	47.50	38.02	31.15	34.13

Table 3: Percentage of metal ions removed from waste water of Kushal Metals Industry, Jodhpur

pH	Fe ²⁺ (%)	Zn ²⁺ (%)	Cu ²⁺ (%)	Cd ²⁺ (%)	Pb ²⁺ (%)
2	62.35	63.56	63.43	57.00	51.56
3	67.24	67.76	69.24	61.68	57.81
4	72.12	73.31	72.88	68.22	66.40
5	75.86	77.21	76.99	73.83	71.87
6	79.59	81.10	81.11	79.43	75.78
7	89.65	85.90	87.40	83.17	82.03
8	82.18	82.60	79.17	75.70	77.34

CONCLUSION

The findings demonstrated that pH 7.0 produced the greatest K_d (distribution coefficients) values for all metal ions under examined. The MSSAHA resin absorbed the most Fe(II) ion from the industrial wastewater. The pH has been discovered to have a significant impact on the metal ion distribution coefficient (K_d). The pH was shown to affect adsorption. It was discovered that MSSAHA resin works well as an adsorbent to take harmful metal ions out of industrial wastewater. At pH 7.0, the best outcomes were obtained. Therefore, MSSAHA resin is advised for treatment of effluents having harmful heavy metal ions. Rathore and Singh (2023) studied on guar gum diamino benzoic acid (GDABA) resin for elimination of hazardous waste metal ions from industrial effluents²⁹. They have reported results on GDABA resin for the elimination of Pb²⁺, Cd²⁺ and Zn²⁺ ions from effluents of Steel Industries in Jodhpur, Rajasthan (India). Anju *et al.*, (2023) studied on tamarind 2-gydoxy-2-methyl butyric acid (THMBA) resin for elimination of hazardous metal ions from industrial effluents³⁰. They have reported results on Tamarind kernel powder (TKP) for their good metal sorption properties and found to have potential for waste management. THMBA resin has been employed for the elimination of Zn²⁺, Pb²⁺, and Cd²⁺ ions in aqueous solution of

effluents of arid region of, with special emphasis in and around Pali district. Due to its affordability, environmental friendliness, and efficiency, the removal of heavy metal ions with MSSAHA resin is currently regarded as one of the most promising techniques. According to the research, harmful metal ions such Fe²⁺, Cd²⁺, Pb²⁺, Cu²⁺, and Zn²⁺ may be selectively removed from industrial settings using MSSAHA resin. Additionally, it works well as an ion exchange for heavy metals like Fe, Cd, Pb, Cu, and Zn, among others. Because the newly created MSSAHA resin is hydrophilic and biodegradable, it may be simply disposed of after effluent treatment without causing any environmental issues. As a result, the current experiment demonstrates that newly synthesized MSSAHA Resin may be utilised to remove harmful heavy metal ions from industrial wastewater in an efficient manner.

ACKNOWLEDGMENT

Authors are thankful to Head, Department of Chemistry, faculty of Science, Jai Narain Vyas University, Jodhpur, Rajasthan, for providing necessary laboratory facility.

Conflict of Interest

Authors have no conflict of interest.

REFERENCE

1. Florea, A.M.; Büsselberg, D. *Biometals.*, **2006**, 19(4), 419-427.
2. Liu, J.G.R.A.; Goyer, R.A.; Waalkes, M.P. 7th ed. New York: McGraw-Hill, 2008, 931-979. Wang, Y.; Ding, L.; Yao, C.; Li, C.; Xing, X.; Huang, Y.; Gu, T.; Wu, M.; *Sci. China Mat.*, **2017**, 60(2), 93-108.
3. Silva, J.E.D.; Paiva, A.P.; Soares, D.; Labrincha, A.; Castro, F. *J. Hazard. Mater.*, **2005**, 120(1-3), 113-118.
4. Holmes, R.R.; Hart, M.L.; Kevern, J. T. *J. Contam. Hydro.*, **2017**, 196, 52-61.
5. Yang, X.; Liu, L.; Zhang, M.; Tan, W.; Qiu, G.; Zheng, L. *J. Hazard Mater.*, **2019**, 374, 26-34.
6. Bashir, A.; Malik, L.A.; Ahad, S.; Manzoor, T.; Bhat, M.A.; Dar, G.N.; Pandith, A.H. *Environ. Chem. Let.*, **2019**, 17(2), 729-754.
7. Yang, K.; Wei, W.; Qi, L.; Wu, W.; Jing, Q.; Lin, D.; *RSC Advances.*, **2014**, 4(86), 46122-46125.

8. Saravanan, D.; Gomathi, T.; Sudha, P.N. *Int. J. of boil. Micromole.*, **2013**, *53*, 67-71.
9. Gao, Y.; Chen, X.; Zhang, J.; Yan, N. *Chem Plus Chem.*, **2015**, *80*(10), 1556-1564.
10. Upadhyay, U.; Sreedhar, I.; Singh, S.A.; Patel, C.M.; Anitha, K.L. *Carbo. Pol.*, **2021**, *251*, 117000.
11. Wang, J.; Chen, C. *Bioresou. Tech.*, **2014**, *160*, 129-141.
12. Wang, J.; Liu, M.; Duan, C.; Sun, J; Xu, Y. *Carbo. Pol.*, **2019**, *206*, 837-843.
13. Pei, X.; Gan, L.; Tong, Z.; Gao, H.; Meng, S.; Zhang, W.; Wang, P.; Chen, Y. *J. Hazard Mater.*, **2021**, *406*, 124746.
14. Fakhre, N.A.; Ibrahim, B.M. *J. of Hazard. Mater.*, **2018**, *343*, 324-331.
15. Kołody ska, D.; Krukowska, J.A.; Thomas, P. *Chem. Eng. J.*, **2017**, *307*, 353-363.
16. Tounsadi, H.; Khalidi, A.; Abdennouri, M; Barka, N. *J. Tai. Inst. Chem. Eng.*, **2016**, *59*, 348-358.
17. Ma, J.; Fang, S.; Shi, P.; Duan, M. *Carbo. Pol.*, **2019**, *223*, 115137.
18. Li, X.; Wang, X.; Han, T.; Hao, C.; Han, S.; Fan, X. *Int. J. Bio. Macromole.*, **2021**, *175*, 459-472.
19. Saya, L.; Malik, V.; Singh, A.; Singh, S.; Gambhir, G.; Singh, W.R.; Chandra, R.; Hooda, S. *Carbo. Pol.*, **2021**, *261*, 117851.
20. Kumar, S.A.; Sujatha, E.R.; *Carbo. Pol.*, **2021**, *265*, 118083.
21. Gunatilake, S.K.; *Methods*, **2015**, *1*(1), 14.
22. Mitra, S.K.; *Acta Hortic.*, **2016**, *1111*, 287-296.
23. Bangar, S.P.; Kumar, M.; Whiteside, W.S. *Int. J. bio. Micromole.*, **2021**, *183*, 1807-1817.
24. Lal, M.; Gangotri, KM; *Int. J. Energy Res.*, **2022**, *46*(14), 19538-19547.
25. Dim, PE.; Termtanun, M.; *Applied Science and Engineering Progress.*, **2021**, *14*(3), 511-524.
26. Antar, AA.; Alsofiany, AA.; Harun, MYB.; *Journal of Applied Science and Engineering.*, **2022**, *26*(4), 475-484.
27. Singh, A.V.; Sharma, N.K.; Rathore, A.S. *Environ. L Tech.*, **2012**, *33*(4), 473-480.
28. Rathore, M., Singh, AV.; *Orient. J. Chem.*, **2023**, *39*(1), 216-221.
29. Anju; Prakash, C.; Choudhary, GK.; Kumari, S.; Choudhary, M.; Chowdhary, V.; *Orient. J. Chem.*, **2023**, *39*(2), 505-510.