

Removal of Heavy Metal Ions in Produced Water Using Cation Exchange Resins From Formaldehyde Polymerized Peanut Testa (*Arachis Hypogaea* L.) Extract Catechins

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Abstract: Peanut testa extract catechins were polymerized with formaldehyde and subsequently functionalized with chlorosulphonic acid. The produced resins were characterized by Fourier Transform Infrared spectroscopy (FTIR), cation exchange capacity, point of zero charge and physical properties determinations. New IR absorption bands due to SO_3H stretching vibrations ($1345cm^{-1}$), stretching ($1325cm^{-1}$), asymmetric ($1180cm^{-1}$) and symmetric stretching ($1032cm^{-1}$) vibrations of the $O=S=O$ (sulfone) group were seen. The results obtained show that the cation exchange capacity of formaldehyde cross-linked peanut testa extract increased significantly from 4.23 to 6.67 meq/g after functionalizing with chlorosulphonic acid. Quantitative removal of Cu^{2+} , Fe^{2+} and Zn^{2+} in the produced water was achieved using both formaldehyde cross-linked (F-PTE) and chlorosulphonic acid functionalized peanut testa extract (FS-PTE). The percentages of Cu^{2+} , Fe^{2+} and Zn^{2+} removed by untreated peanut testa, peanut testa extract and the synthesized resins (PT, PTE, F-PTE, FS-PTE) were determined by batch technique using atomic absorption spectrophotometry (AAS) and were found to be: 13.8%, 7.08%, 54.8% and 68.3%; 15.2%, 6.7%, 64.1% and 78.7% and 16.6%, 12.4%, 56.6% and 67.8% respectively. The results which compared with those of a commercial ion-exchange resin (Bio-Rex 70) showed that formaldehyde cross-linked and chlorosulphonic acid functionalized - formaldehyde cross-linked peanut testa extract cation exchange resins are effective in decontaminating metal ion laden produced water.

Keywords: Peanut testa extract, crosslinking, functionalizing, heavy metals, cation exchange capacity

I. Introduction

Water which is one of the most valuable natural resources is essential to all living things (Tansel, 2008) and makes up 50-97% of the weight of all living things (Bello *et al.*, 2014 and Mustafa *et al.*, 2013; UNEP Joint report, 2010). Besides being the medium for the transport of nutrients and waste matter in organisms (Tansel, 2008), it is an important source for agriculture, industry, transportation and many other human activities (Kumar, 2004 and Walakira, 2011). It's quality is important to man not only because it is essential for her welfare (Chennakrishnan *et al.*, 2008) but because scientific reviews show notable links between diseases and the amounts and types of fluids consumed, the health-promoting properties of nutrients which are taken together with water, its best intake levels and consumption patterns (Balajiet *et al.*, 2014; Tansel, 2008 and Kumar, 2004).

Produced water (PW) which is the large volume of water co-generated with oil and gas during sub-surface production contains numerous substances including several heavy metal ions Zn^{2+} , Fe^{2+} , Cu^{2+} etc. (Iggunnu and Chen, 2012 and Barakat, 2011). The oil and gas industry produces approximately 250 million barrels of this water daily across the globe out of which over 40% is discharged into the environment (Ojedokun and Bello (2015) and Iggunnu and Chen, 2012) with shabby treatment leading to the migration of metals across the food chain and resulting in many problems which are traceable to the ecosystem (Qaiser *et al.*, 2007). H. R. H. Prince Alexander of the Netherlands said that the over 80% untreated wastewater discharged into water bodies is the major setback in the effort to win the battle against filth and that it impacts negatively on human health, agriculture, socio-economic development (Aklet *et al.*, 2013), environmental management and sustainability of the ecosystem (UNEP Joint report, 2010). Galadima *et al.*, (2011); Ibeto and Okoye, (2010) and Goyal, (2015) reported the results of studies which show that drinking water sources of various communities are contaminated with heavy metals.

Heavy metals are not metabolized into safe end products in the body rather they build up and interfere with physiological functions resulting in many systemic diseases in man and other living organisms (Maigari *et al.*, 2016 and Anim-Gyampo *et al.*, 2013). Igweet *et al.*, (2013) sited chronic pollution which limits breeding and reproduction in seabirds as an example of the consequences of discharged PW. PW can be harnessed, sufficiently treated to remove contaminant metal ions and supplied as potable water for use in industries, agriculture and to arid regions after complementary treatments have been performed to remove other polluting substances. Iggunnu and Chen, (2012); Abreu *et al.*, (2012); Ayadet *et al.*, (2010); Ayad and Al-Razaq, (2012); Azetsu-Scott *et*

al., (2012); Igwe *et al.*, (2013); Kanu and Oji, (2012); Dune *et al.*, (2013); Dune and Ezeilo, (2012); Obuzor and Ejimozor, (2011) and Oboh *et al.*, (2009) used various techniques to remove heavy metal ions in PW. In the present study, polyphenols in the extract of peanut (*arachishypogaea l.*) test was chemically transformed into cation exchange resins by first crosslinking with HCHO (F-PTE) and subsequently functionalized using ClSO₃H to improve its metal ion uptake ability. The prepared resins were used to remove Zn²⁺, Cu²⁺ and Fe²⁺ in PW and the results obtained were compared with those obtained using a commercial ion exchange resin; Bio-Rex 70.

II. Materials And Methods

All the chemicals used in the study were of analytical grade, purchased from IDEX Scientific Supply Company and were used without further purification.

Collection of adsorbate

The PW sample was collected from a hydrocarbon production facility in Rivers State, Niger Delta region, Nigeria at a point before discharge or re-injection (Wash Tank). After collecting in a sterilized plastic bottle, dilute HNO₃ was added before covering and transporting to the laboratory.

Sampling

Freshly baked peanut testa waste was collected from a commercial point in Alakahia, near Port Harcourt, Rivers State, Nigeria. After identification by the Department of Plant Science and Biotechnology of the University of Port Harcourt, it was thoroughly washed with cold deionized water (DI H₂O), air-dried for one week, dried further in the oven at 110°C for 2 hrs before grinding to 250µm particle size. This was labelled peanut testa (PT).

Extraction of polyphenols from PT

Polyphenols were extracted from 600g of PT using 1L of acetone by means of a Soxhlet extractor. After recovering the acetone by distillation using a water bath, the concentrated extract was washed with hexane and DI H₂O to strip adhering oil and acetone before drying in the air. The yield of extract was 43.58%. It was ground to a fine powder in a laboratory mortar and labelled peanut testa extract (PTE).

Preparation of calibration solutions

A multi-elements primary stock solution containing 100 ppm each of Zn²⁺, Fe²⁺ and Cu²⁺ was prepared by dissolving 0.1100, 0.1245 and 0.0785g of ZnSO₄·7H₂O, FeSO₄·7H₂O and Cu(CH₃COO)₂·H₂O respectively in a 250ml standard flask and diluting to volume with DI H₂O. 1ppm, 2ppm, 4ppm and 5ppm calibration solutions were then prepared.

Synthesis of HCHO–PTE (F-PTE) Resin

The method of Yurtsever and Sengil, (2009) was modified and adopted for the synthesis of F-PTE. PTE (25g) was first polymerized for 1 hour at room temperature (RT) using 50ml of 37% HCHO as a crosslinking agent and subsequently stirred in 50ml of 10% NaOH for 6 hours at 65°C. Thereafter, the flask was brought down, the thick gel crushed into tiny beads before filtering. The product was successively washed with DI H₂O, 100mL of 0.1M HCl solution, DI H₂O again until the filtrate tested neutral to methyl red indicator. It was finally washed with 100mL of pure CH₃OH and dried for 10 hours at 60°C to yield 73.82% of F-PTE resin.

Sulphonation of HCHO Crosslinked–PTE with (FS-PTE)

The method of United States Patent No 2,621,164 was modified and adopted for the functionalizing of F-PTE with ClSO₃H (CSA). Precisely, 10g of F-PTE resin was stirred to homogeneity in 40mL of dichloromethane (DCM) and heated in a water bath for 1 hour at 95°C. Thereafter, a freshly prepared solution containing 5mL of chlorosulphonic acid (CSA) and 10mL of DCM was added in drops and the mixture continued to heat under reflux for additional 1.5 hrs at which point the gel formed did not allow the magnetic bead to dart freely. The set-up was brought down. When the flask had cooled down sufficiently, the content was filtered and the residue liberally washed with DI H₂O until the filtrate tested neutral to methyl red indicator. It was finally washed with 100mL of CH₃OH and later dried for 10 hours at 60°C to yield 69.39% of FS-PTE.

Characterization

The synthesized resins were characterized according to the following properties: solubility in common solvents (H₂O and alcohol). Specific gravity (Sp.g), melting Point (M.P.) and the functional groups present were determined by means of a pycnometer, a model 300 conTeCH digital melting point apparatus and an Affinity-1S model Shimadzu Fourier Transform Infrared (FTIR) spectrometer in the range of 400–4000cm⁻¹ respectively. Cation exchange capacity (CEC) and the pH at the point of zero charge (pH_{PZC}) were determined by the standard column and the solid addition methods (Vieira *et al.*, 2014).

Ion exchange studies

PT, PTE, F-PTE and FS-PTE cation exchange resins were converted to the hydrogen ion (H⁺) forms by soaking overnight in dilute HNO₃ and washing to a neutral pH before using for adsorption experiments. For this purpose, 1g each of PT, PTE, F-PTE, FS-PTE and Bio-Rex 70 was separately added to 50mL of PW held in a 100mL plastic bottle. The concentration of the metal ions in the PW had been determined and was reduced by diluting with DI H₂O which served as the calibration blank. The pH of the mixture was adjusted to 6.0 ± 0.5

with either 0.1M HCl or 1M NaOH before screwing on the bottle caps. The bottles were agitated at 150rpm (revolutions per minute) on a Nuve SL 250 horizontal bench shaker for 2hrs at RT. At the end of the process, the bottles were disengaged and the suspensions were rapidly filtered over a whatman No. 2^V folded filter paper. The concentrations of Fe²⁺, Cu²⁺ and Zn²⁺ present in the filtrates were determined by the use of Atomic Absorption Spectrophotometer (AAS) model PG A500. The amount of each metal ion removed from the solution by the adsorbent at equilibrium Q_e (mg/g), was computed using the model:

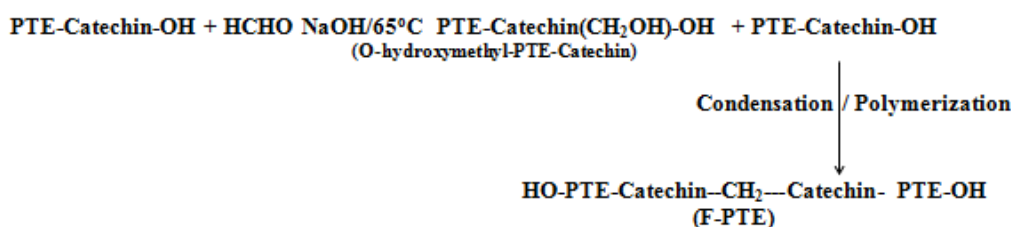
$$Q_e = \left[\left(\frac{C_o - C_e}{W} \right) \right] x V \quad 1$$

Where; C_o and C_e are the initial concentration and the concentration (mg/L) of the metal ion in the PW at equilibrium while V and W are the volume of the PW and the mass of the adsorbent (g) used respectively. Atomic absorption measurements were carried out in triplicate runs and the average of two readings was reported in percentage.

III. Results And Discussion

Formation of F-PTE

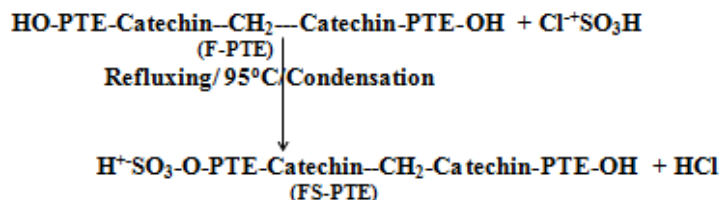
Two steps were involved in the base catalyzed polymerization of PTE-catechin units with HCHO to yield the high temperature resistant and free flowing F-PTE resin. The first step; the methylation step produced the O-hydroxymethyl-PTE (polyphenol) which reacted with a PTE molecule, eliminated a molecule of H₂O with the formation of a methylene (-CH₂-) bridge. This is illustrated in scheme 1 below.



Scheme 1: Reaction scheme for the formation of F-PTE resin

Functionalizing of F-PTE with ClSO₃H (FS-PTE)

The sulphonation of F-PTE by CSA was a one-step condensation reaction in which CSA donated the active sulphonic acid group (HSO₃⁻) to the acceptor OH group of F-PTE catechin units to form a carbon-oxygen-sulfur (C-O-S) bond. The path to the formation of the bead-like FS-PTE is shown in Scheme 2 below:



Scheme 2: Reaction scheme for the formation of FS-PTE resin

Table 1: Physicochemical Properties of PT, PTE, F-PTE, FS-PTE resins and Bio-Rex 70

Sample Id	Sp.g(g/L)	M.P.	H ₂ O Solubility	Solvent Solubility	pH _(zpc)	CEC
PT	1.17	Stable above 300°C	Insoluble	Partial	6.97	0.62
PTE	1.33	170°C	Insoluble	Soluble	7.01	0.58
F-PTE	1.43	Stable above 300°C	Insoluble	Insoluble	5.14	4.23
FS-PTE	1.29	Stable above 300°C	Insoluble	Insoluble	4.54	4.67
Bio-Rex 70	0.7	Decomposed above 100°C	Insoluble	Insoluble	2.02	10.2

Physicochemical Properties of PT, PTE, F-PTE, FS-PTE resins and Bio-Rex 70

The properties of PT, PTE, F-PTE, FS-PTE resins and a commercial ion exchange resin; Bio-Rex 70 according to M.P., solubility, Sp. g, CEC and pH_(zpc) charge are reported on Table 1.

Melting Point

Apart from PTE which decomposed at 170°C the rest of PT, F-PTE and FS-PTE resins were stable above 300°C. Resistance to heat is an attribute of cross-linked resins and thermosetting polymers. The -CH₂- bridges which were formed during the hydroxymethylation of PTE catechin units resulted to cross-linked products (F-PTE and FS-PTE) which were resistant to heat.

Solubility Test

PTE soaked and retained H₂O during the study but did not dissolve in it. This is because the molecules of condensed tannins, the group to which PT polyphenols (catechins) belong possess a highly ordered supra-molecular structure (Bergh, 2011). PTE catechin molecules are held together by H-bonds which were made stronger by crosslinking with HCHO and the esterification with CSA. Bergh, (2011) and Peters, (2006) said that such resins are generally insoluble in H₂O and solvents because the polymer units in the molecular chains which are covalently joined do not interact freely with solvents. PT and PTE were insoluble in H₂O but displayed partial and complete solubility in organic solvents respectively because there was no crosslinking hence solvent/substrate interaction was unlimited. Vieira *et al.*, (2014) and Wan-Ngah and Hanafiah, (2008) said that the physicochemical properties of plant constituents are permanently altered when new functional groups are incorporated into the biochemical structure. Pangeniet *al.*, (2014) observed that the leakage of total organic carbon (TOC) from persimmon waste (PW) was suppressed after cross-linking with H₂SO₄. The newly introduced functional groups altered the molecular structure and the types of bonds in F-PTE and FS-PTE. This is the reason why PTE which was soluble in acetone before chemical modification would neither dissolve in it nor any of the tested solvents after modification.

Cation Exchange Capacity (CEC)

The CEC of a substance is the ability of that substance to exchange positive ions with the environment which it interacts with (Fabio and Reinaldo, 2012). It is an estimate of the free ions of opposite charge which can be replaced with the cations and equivalent to the number of H⁺ released from the substance when a solution of a neutral salt is poured through it (Singh and Kumawat, 2012). The CEC values of PT, PTE, F-PTE and FS-PTE listed on Table 1 show that the CEC of the synthesized resins were higher, they possessed more replaceable H⁺ and consequently would be able to exchange for more metal ions in solution than the starting materials

Point of Zero Charge (pH_{pzc})

It is defined as the pH of an adsorbent-adsorbate suspension at which the functional groups on the surface of the adsorbent do not contribute to the pH of the solution (Onwu and Ogah, 2010). As shown in Table 1, the pH_(zpc) of PT, PTE, F-PTE and FS-PTE cation exchange resins was below the pH (6.0 ± 0.5) of the solution in which the adsorption experiment was performed. Since the surfaces of a metal ion adsorbent with acidic pH (pzc) value are dominated by acid rather than basic groups (Jorgetto *et al.*, 2014), it shows that the F-PTE and FS-PTE cation exchange resins have the capacity to work over a wide pH range. The -CH₂-, SO₃H and O=S=O groups incorporated onto PTE during the modification caused a decrease in the pH (pzc) values of the new products (F-PTE and FS-PTE) derived from it. This indicates that each resin attracted the highest number of positive charges at the pH that produced negative charges on its surface. This pH is wide (> 4.23) for F-PTE and FS-PTE hence, the improvement in their ability to remove metal ions in the PW over PT and PTE. Veira *et al.*, (2014) stated that the attraction of positive charges by maleic acid modified *babasuepicarp* (BEM) was only favorable when the pH of the adsorbate solution was higher than the pH (pzc) value of 6.45 because the formation of negative charges (which were necessary for adsorption of metal ions onto the biomass) on the surface of BEM occurred at this pH.

Table 2: Characteristic Bands in the FTIR Spectra of PT, PTE, F-PTE and FS-PTE

S/No	Frequency	Origin/Functional Group	Inference
1	3423/3431/1377	Typical of the -OH group	-O-H (stretching, in and out of plane movements)
2	1142/926/928	-C-H stretch	Probably due to the -C-H bonds of the starting materials
3	1629/1528	-C=C- in a ring	May be from the -C=C- bonds of the polyphenols in the starting materials
4	1160/1034	-C-O-C- of large cyclic ethers	Likely to come from the -C-O-bond of the ether bearing ring of the polyphenol units of PTE
5	1325/1140	Stretching vibration of a sulfone O=S=O	May be due to a part of the SO ₃ H group created on the PT polyphenol
6	1345	Stretching vibration of SO ₃ H group	
7	1180	Asymmetric stretching vibration of O=S=O	IR bands in the region of 1180cm ⁻¹ and 1032cm ⁻¹ are characteristic bands of SO ₃ H containing compounds
8	1032	Symmetric stretching vibration of O=S=O	

FTIR Spectra of PT, PTE, F-PTE and FS-PTE

The FT-IR spectra of PT, PTE, F-PTE and FS-PTE cation exchange resins are described on Tables 2. The broad band at $3431/3423\text{cm}^{-1}$ and the medium peaks at $1377/617\text{cm}^{-1}$ are probably due to the stretching and the bending movements of the -OH groups present in the polyphenol (five in catechin) units of PT and PTE. The peaks at $2926/2928\text{cm}^{-1}$ and 1142cm^{-1} are due to the stretching and bending vibrations of the Sp^3 (-C-H) of the ether bearing middle ring in the catechin units. The stretching movement by the -C=C- bonds in the side rings showed as peaks at $1629/1528\text{cm}^{-1}$ and while the stretching vibration by the -C-O-C- bond of the cyclic ether middle ring occurred at $1160/1034\text{cm}^{-1}$, its -C-H stretching movement showed at $823/668\text{cm}^{-1}$. The main differences between the spectra of PTE and F-PTE are the intensities of the -CH₂ and -OH groups which were larger in the F-PTE. The reason is that the observed intensities are the combined intensities of the many separate units which were brought together by the crosslinking process to form the rigid large units of F-PTE. The intensity of the -CH₂ band in PTE was 1.15% while it was 1.99% in F-PTE. On the other hand, the intensity of the -OH bands was lower in the spectrum of FS-PTE than its intensity in F-PTE. This is explained by the fact that some of the -OH groups had been used in the sulphonation process which resulted in the creation of the sulfone (O=S=O) group on F-PTE units. In addition to these bands, FS-PTE showed additional IR peaks at $1395, 1373, 1363$ and 1352cm^{-1} . O=S=O, sulphonic acid (-O-SO₃H) and sulfonyl (R-S(=O)₂-R) groups show stretching vibrations around 1300cm^{-1} in the IR region of the electromagnetic spectrum. IR bands in the regions of 1180cm^{-1} and 1032cm^{-1} are characteristics of the symmetric and asymmetric stretching vibrations of the O=S=O group and is typical of HSO₃⁻ containing compounds. Bands at $1325/1140$ are due to stretching vibrations of the O=S=O while the one at 1345 is from the stretching vibration of the HSO₃⁻ (Meyer, 2000).

Adsorption of metal ions in PW by PT, PTE, F-PTE, FS-PTE and Bio-Rex 70

Table 3 Mean adsorption and comparison of the efficiencies of PT, PTE, F-PTE, FS-PTE with Bio-Rex 70 in removing Cu²⁺, Fe²⁺ and Zn²⁺ in PW

Heavy metal	PT	PTE	F-PTE	FS-PTE	Bio-Rex 70
	Initial (ppm) / % Removed	Initial (ppm) / % Removed	Initial (ppm) / % Removed	Initial (ppm) / % Removed	Initial (ppm) / % Removed
Cu	9.6/13.8	9.6/7.08	9.6/54.8	9.6/68.3	9.6/61.5
Fe	17.5/15.2	17.5/6.7	17.5/64.1	17.5/78.7	17.5/69.1
Zn	22.5/16.6	22.5/12.4	22.5/56.6	22.5/67.8	22.5/67.1

As shown on Table 3, FS-PTE removed more of the metal ions in PW than PT, PTE, F-PTE and Bio-Rex 70. This may be due to the presence of the polar -SO₃H group on the resin molecule. The group is high in electron density because of the lone pair of electrons on the O=S=O group. Alexandratos and Natesan, (1999) observed that the biomass which they immobilized by incorporating -SO₃H groups onto its aromatic ring structure complexed over 90% of the metal ions more rapidly in acid solutions. Nada *et al.*, (2009) reported higher Zn²⁺, Pb²⁺, Fe²⁺, Ni²⁺ and Cr²⁺ removal efficiencies by sulphonated corn cob over the unmodified one. The ability of F-PTE resin to remove more metal ions than PT and PTE is explained by the fact that its metal ion removing ability is a summation of the metal ion removing abilities of the individual polyphenol/catechin units which contributed to its formation. Wan-Ngah and Hanafiah, (2008) explained that the process of chemical modification increases the number of active binding sites on an adsorbent by forming new functional groups, improving its adsorption capacity and impartation of better ion exchange properties which ultimately favour the uptake of metal ions. Agiri and Akaranta, (2009) discovered that their -SO₃H dye treated cassava mesocarp removed more Cu²⁺ and Zn²⁺ than the undyed one and explained that the (2, 7-naphthalene disulphonic acid-5-[(4, 6-dichloro, 1, 3, 5-triazine-2-yl)amino]-4-hydroxyl-1,3-disulpho-7-naphthalenyl) azo-tetra sodium salt) dye with which they modified the cassava mesocarp adsorbent introduced -SO₃H groups on the surface of the adsorbent. In collaboration with Ogali *et al.*, (2008), they said that the presence of the -SO₃H groups improved the acidity of the adsorbate solution and in addition to the -COOH, phenolic and -OH groups of cassava mesocarp was responsible for the greater affinity of Cu²⁺ and Zn²⁺ to the -SO₃H dye treated cassava mesocarp over the undyed one. This may also be the reason why FS-PTE removed more of the divalent metal ions in the PW than F-PTE. The results also showed that PT removed more of each of the metal ions than PTE. Since PTE consisted of the extracts only, it is possible that the metal ions could not be held firmly to the adsorption sites of the jelly polyphenols of PTE, whereas, they were bound to PT by a combined strength of the rough macroporous and smooth jelly polyphenol units. Nada *et al.*, (2009) explained that cellulose containing agricultural wastes is more effective ion exchange substrates because the metal ion removal abilities are enhanced by their fibrous structure. The removal of metal ions by unmodified biomass is a result of contributions from the entire biochemical constituents and not just a single component such as catechin which is the chief constituent of the polyphenol extractive; tannin that is present in PTE. Laszlo and Dintzis, (1994) recognized that crop residues like catechins are good adsorbents for divalent metal ions, but they agreed with Chen *et al.*, (2011) and

Anggraeniet *al.*, (2008) that the performances of the residues are limited by low ion exchange capacity and poor physical stability.

IV. Conclusion

The study shows that good adsorbents for the removal of Fe^{2+} , Cu^{2+} and Zn^{2+} in produced water can be obtained from resins gotten from peanut testa which is usually thrown away. The results of the investigation showed that modified PTE cation exchange resins (F-PTE and FS-PTE) compared favourably with the commercial ion exchange resin (Bio-Rex 70) in the removal of these metals. And thus, would help to save the money that is currently spent in procuring such resins. The research supports the potential application of this technique in the recovery of wastewater, mitigating the burden of water scarcity and waste disposal while protecting the environment from pollution by heavy metals.

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