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Preparation of recycled polystyrene derivatives to remove heavy metal ions from contaminated water

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ABSTRACT

In recent years, numerous researchers have concentrated on the process of turning waste into usable materials. Polystyrene and its modifications have received great attention over the past few decades due to their outstanding ion exchange behavior toward various toxic heavy metals in aqueous solutions. Therefore, this study is concerned with the preparation of three different cationic polymeric resins for the removal of Pb^{2+}, Cd^{2+}, and Fe^{3+} heavy metal ions from their contaminated water samples based on the sulfonated single-used polystyrene teacup waste (SPS), which was used to prepare sulfonated polystyrene-g-acrylamide monomer (SPS-g-Acryl) and sulfonated polystyrene-g-chitosan (SPS-g-Chit) using commercial chitosan (DD=85%) originally extracted from shrimp cortex. The concentrations of the selected heavy metal ions were measured before and after each experiment with a flame atomic absorption spectrometer (F-AAS). The analytical studies started by exploring the influence of pH (2, 4, 6, and 8) on removing the heavy metal ions Pb^{2+}, Cd^{2+}, and Fe^{3+} from their aqueous solutions. The obtained results revealed that as the pH of the analyzed ion solution is increased, the removal efficiency for ions increases. All three resins (SPS, SPS-g-Acryl, and SPS-g-Chit) had different removal efficiencies for the investigated ions, with SPS-g-Chit resin being the best in both batching and column loading methods, and they could be compared in the following order: SPS-g-Chit > SPS-g-Acryl > SPS, and it could be reused after regeneration.

1. Introduction

Water is one of the most crucial natural resources for the survival of all living forms, food security, economic development, and welfare. De-pollution is a gift from Mother Nature to the globe that cannot be replicated for many purposes and costs a lot to ship [1]. The world's freshwater habitats represent about 5% of the Earth's land area but contain 2.84 billion km3 of freshwater. Only one percent of the earth's water is in rivers and streams. Despite the small

amounts, the presence of large volumes of flowing water is critical. The exponential development of the population and increased industrialization have led to an enormous rise in freshwater consumption in recent decades. Heavy metal pollution of the water environment threatens human health in most countries. It has increased recently along with economic development and population growth, primarily from mining, electroplating, and the production and shipment of batteries. They damage the body, including the skin, lungs, head, liver, and kidneys, and cause tumors, birth defects, and other conditions. Consequently, the quality of drinking

water is declining, and there is a need for better water management and a method for preventing water contamination and providing pure water [2]. This explains why, for the government and experts, water contamination has become a study subject [3]. Both the water and its geographic and seasonal supply, as well as their surface and groundwater content, are very important for climate, economic growth, and development. Because of increased population growth, urbanization, expansion of agriculture, and more, these factors influence water quality. Polluted water affects the lives of today's people and those of future generations, as its effects continue to be long-lasting. If water is contaminated in a city, all livelihoods and citizens are confronted with drinking poisoned water because they have no alternative. The damage to the human body (skin, lungs, head, liver, and kidneys) causes tumors, birth defects, and other conditions. We concluded that the quality of drinking water is declining because of increasing population, agricultural practices, and industrialization, and there is a need for better water management and a method for preventing water contamination and providing pure water [2].

Due to the issues above, a substantial focus has recently been placed on developing more effective, less expensive, and long-lasting wastewater treatment systems that do not add to environmental stress or pose a health risk to humans. In recent years, extensive testing has been done to develop alternative and cost-effective water and wastewater technologies. Coagulation, membrane processes, adsorption, dialysis, flotation, osmosis, and photocatalytic degradation are some methods used to remove hazardous substances from water. However, as seen in Figure 1, various sources of pollutants are in the water [4].

Many methods have been studied to treat heavy metals from wastewater; these can be chemical, physical, or biological. The most promising technologies to overcome these constraints are adsorption and ion exchange [5,6]. Given the various industrial applications of large quantities of ion exchange resins consumed after being used for specified periods, depending on the operating conditions, they should be replaced by new ones [7,8]. This prompted us to look for a less expensive alternative method of providing it. In
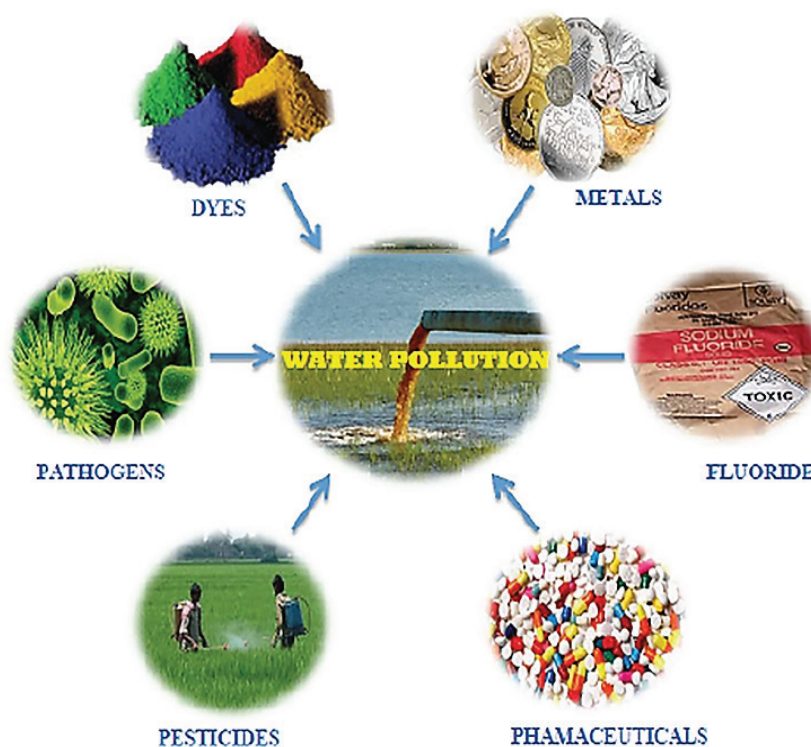

Fig. 1. Some sources of pollutants in water [4]

previous work, sulfonation and grafting acrylamide monomer and chitosan polymerization synthesized two ion exchange resins from recycled polystyrene single-used teacup waste [9]. They were used as ion exchangers to determine the total hardness of tap water. Both prepared resins were characterized by FTIR, which confirmed the properness of the sulfonation and grafting processes on sulfonated polystyrene, respectively. The grafting process causes an increase in the efficiency of the sulfonated polystyrene resin in removing the hardness of tap water. Polystyrene sulfonating reduces the volume of solid waste and contributes to environmental cleanliness.

The results of our investigation into the technical viability are presented in this research using sulfonated polystyrene-g-acrylamide (SPS-Acryl). Sulfonated polystyrene-g-chitosan (SPS-Chit) derived from polystyrene single-use teacups after sulfonation (SPS) for heavy metal removal in batch experiments and continuous fixed bed column experiments for checking their feasibility if applied in practice are presented in this research. In addition to reducing environmental degradation, recycling this material as an ion exchange material also limits the exploitation of natural resources.

2. Experimental

2.1. Materials and instrument

Sulfuric acid (96%) was used as a sulfonating agent; Chitosan (80 mesh, DD = 85) and acrylamide monomer were used as grafting materials; nitric acid and ammonium hydroxide solution were purchased from Sigma-Aldrich. Cadmium (II) nitrate, iron (III) chloride, and lead (II) nitrate were purchased from Global Chemical Company (L.L.C; GCC) and used as sources for heavy metal ions in pollutant samples. The concentrations of the Pb^{2+}, Cd^{2+}, and Fe^{3+} heavy metal ions were measured with a flame atomic absorption spectrometer (F-AAS, Varian AA240 FS, USA). The IKA magnetic stirrer was purchased from Sigma Aldrich (IKA®C-MAG MS; SKU: Z671835, Germany). Digital pH meter purchased from Thermo Fisher Scientific (USA).

2.2. Sulfonated polystyrene preparation (SPS)

The single-use polystyrene teacups were collected and washed several times with tap and distilled water before drying at room temperature. As mentioned in the literature, sulfonated polystyrene and SPS-g-acrylamide monomers were prepared [9,10]. In a 250 mL round bottom flask, 20 g of chopped waste teacups made of polystyrene were added. 50 mL of 96% sulfuric acid was added, and the mixture was continuously stirred at room temperature. The mixture was then refluxed for approximately 4 hours at 60–65°C. Sulfonated polystyrene was obtained through separation and filtration after adding cold, distilled water stopped the reaction. Following a pH-neutralizing wash with distilled water, it was dried at 60°C.

### 2.3. Synthesis of SPS-g-acrylamide resin (SPS-g-Acryl)

SPS-g-acrylamide was prepared by grafting acrylamide monomers onto the prepared SPS. This was done by weighing 5.0 g of SPS resin and placing it in a 100 mL 2-neck round bottom flask filled with 50 mL distilled water and equipped with a magnetic stirrer. After that, 5 g of acrylamide monomer was gradually added. The mixture was stirred at 40 °C for 3 hours to complete the grafting process. The resin was then dried at 60 °C after being rinsed with distilled water to remove any non-grafted monomer [10,11]. Scheme 1 shows the grafting reaction of the acrylamide monomer on the sulfonated polystyrene.

2.4. Synthesis of SPS-g-chitosan resin (SPS-g-Chit)

In a 100 mL round bottom flask, 5.0 g of chitosan was dissolved in 75 mL of 2% acetic acid, and the solution was gradually added to 5 g of SPS. The mixture was then heated for 3 hours at 60–65 °C. The SPS-g-Chit was filtered and rinsed three times with deionized water and acetone after allowing the liquid to cool to room temperature. The white product was dried using a vacuum desiccator [12,13]. The grafting reaction of the chitosan on the sulfonated polystyrene is depicted in Scheme 2.
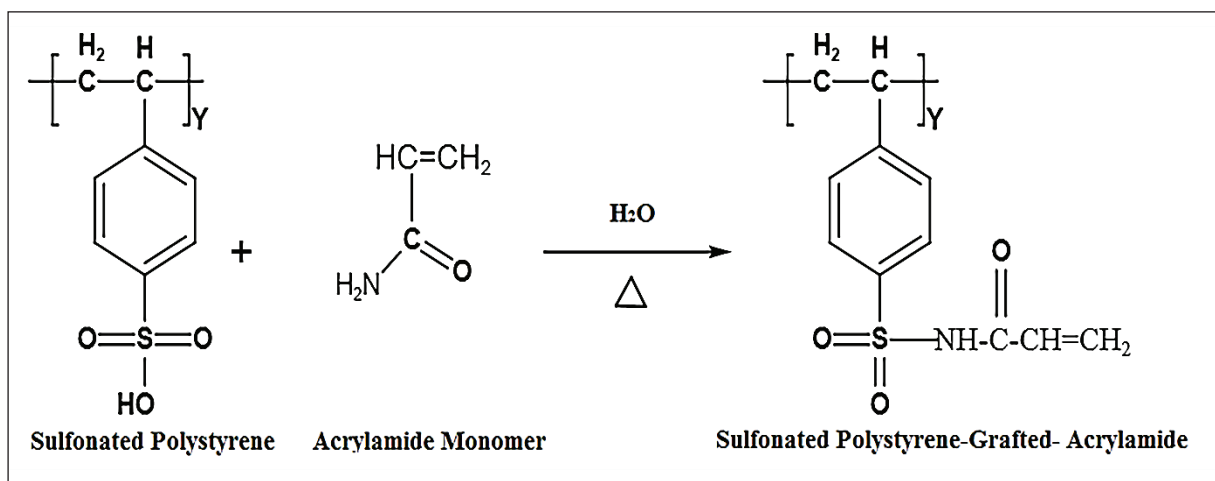
Scheme 1. The chemical equation of grafting acrylamide onto SPS resin
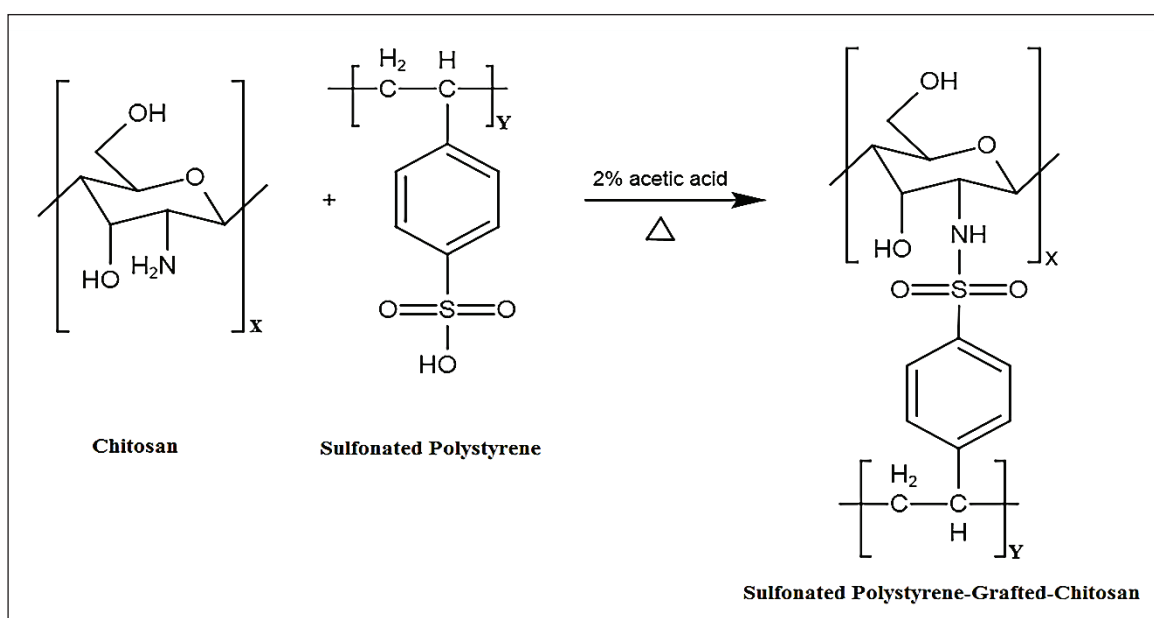
Scheme 2. The grafting reaction of SPS resin with Chitosan

2.5. Preparation of heavy metal ion standard solutions

standard solutions containing different concentrations of the element ions (Pb^{2+}, $Cd^{2+,}$ and Fe^{3+}) were made by diluting 1000 mg L^{-1} stokes solutions of their salts to 50 mg L^{-1} with double-distilled water. The salts of these elements used were $FeCl_3.6H_2O$, $Cd(NO_3)_2.4H_2O$, and $Pb(NO_3)_2$ [14]. All the concentrations of heavy metal ion solutions were measured before and after each experiment with a

Flame atomic absorption spectrometer (Sens, Japan).

2.6. Heavy metal ions removal in batch method

Batch-mode ion exchange experiments were performed in beakers under constant time and temperature conditions [15,16]. The effect of SPS, SPS-g-Acryl, and SPS-g-Chit resins was studied in different pH ranges (2–8) to investigate the changeability and bonding of heavy metal ions (Pb^{2+}, Cd^{2+}, and Fe^{3+}) to the resins.

2.7. Study the effect of the pH on the resins by batch method

One gram of each resin (SPS, SPS-g-Acryl, and SPS-g-Chit) was treated with 25 ml of prepared aqueous solutions of Pb^{2+}, Cd^{2+}, and Fe^{3+} in pH ranges of 2, 4, 6, and 8 [17,18]. Each bottle containing resins was left at room temperature for an hour of shaking (175 rpm min^{-1}). After being filtered, the filtrate was collected in 50 mL of a plastic bottle.

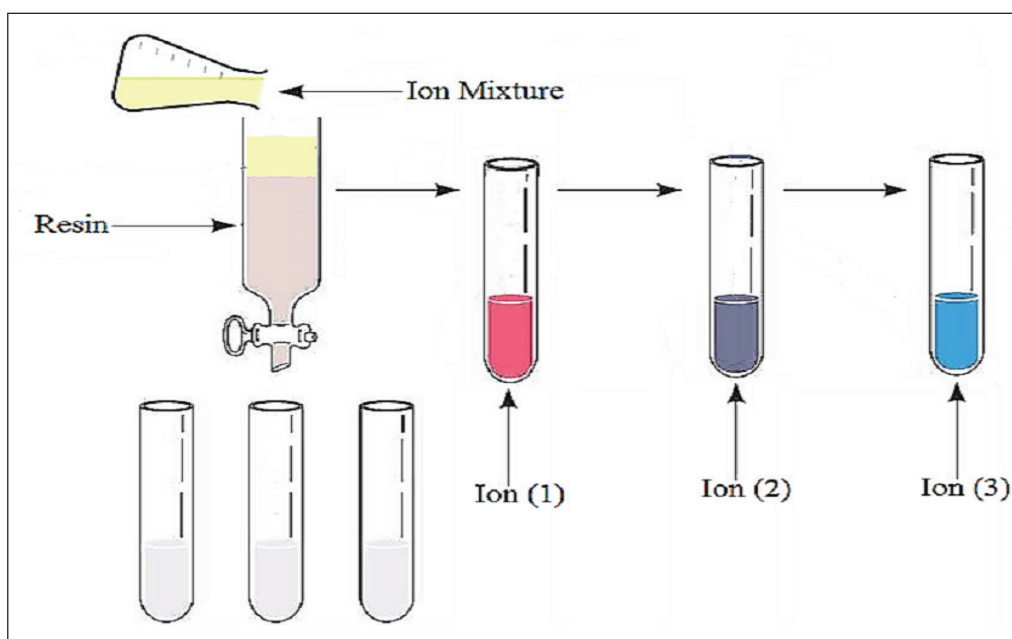## 2.8. Heavy metal ions removal by column method

This experiment was carried out to investigate the practicability of using SPS, SPS-g-Acryl, and SPS-g-Chit resins for heavy metal removal in a continuous flow column [19,20]. The water solution containing a mixture of the three heavy metal ions (Pb^{2+}, Cd^{2+}, and Fe^{3+}) was continuously passed through a vertical glass column with a height of 20 cm and a diameter of 1 cm. The operational parameters were set at a flow rate of 1 mL min^{-1}, an inlet heavy metal concentration of 50 mg L^{-1}, and 10 g of each prepared resin, as shown in Scheme 3. All tests were run continuously until the heavy metal removal efficiency decreased significantly. Finally, the concentrations of the Pb^{2+}, Cd^{2+}, and Fe^{3+} ions were determined with a flame atomic absorption spectrometer (F-AAS)

2.9. Regeneration of the loaded resins

For regeneration experiments, the best-loaded resin with metal ion removal obtained at pH 8 from a column method was chosen. One gram of the loaded resin was treated for a half-hour in a column system with a flow rate of 1 mL per minute with 30 mL of 0.1 N HNO_3 before being washed directly with 30 mL of deionized water and collected in plastic bottle samples [21].

2.10. Examination of single and mixture heavy metal ions by column method

A column with a 15 cm length and a 2.5-mm inner diameter was chosen for the analytical studies. It was then loaded with 1.0 g of SPS, SPS-g-Acryl, and SPS-g-Chit resins, and 25 mL of metal ion solutions (Pb^{2+}, Cd^{2+}, and Fe^{3+}) at a flow rate of 1 mL min^{-1} with a 50 mg L^{-1} concentration at pH 8. A mixture of the three ions (Pb^{2+}, Cd^{2+}, and Fe^{3+}) was prepared in 25 ml with a 16.6 mg L^{-1}, and the pH was adjusted to 8. The column was charged with 1 g of each resin. The mixture of ion solutions was allowed to flow through the loaded column at a rate of 1 mL min^{-1}. The descending solution was collected in portions for each component over an approximately 30-minute interval. The concentrations of the heavy metals were measured with F-AAS.

Scheme 3. The Schematic diagram for heavy metal ions removal by column method

3. Results and Discussion

The sulfonation reaction by sulfuric acid provides sulfonic groups SO_3H^+ attached to the polystyrene backbone chains, giving ion exchange capacity to the polystyrene, which will be a center for the grafted acrylic monomer and chitosan polymer material to make up copolymers attached to the sulfonated polystyrene [10-12]. One advantage of this approach is the ability to precisely modify characteristics by adjusting the grafting or sulfonating conditions. The activation of the backbone polymer, the grafting of a monomer onto the produced polymer and the subsequent functionalization of the grafted polymer are all steps in the graft copolymerization technique of ion-exchange synthesis, yielding a product with high chemical selectivity [22,23]. Because heavy metals are typically produced by known sources, removing them rather than releasing them into the environment is preferable. The ion exchange capacity of the made resins is determined by the nature of the active groups, whose selectivity varies depending on the heavy metal ions and pH, the temperature and concentration employed, the nature of those ions, and the number of active groups. All of these are important in defining pH-dependent changeability. The pH was controlled by dilute solutions of 0.01 N nitric acid and 0.01 N ammonia solution [10]. The effect of the pH on the changeability of the three heavy metal ions (Pb^{2+}, Cd^{2+}, and Fe^{3+}) with the active groups of the prepared resins; SPS, SPS-g-Acryl, and SPS-g-Chit, was investigated by changing the pH from 2 to 8 with an initial concentration of ion solutions of 50 mg L^{-1}. Since metal cations attached to $-SO_3H$ in functional groups were released and H+ ions were added after the ion exchange reaction, the pH after equilibrium was slightly reduced. Therefore, the metal precipitation did not take place [24,25].

3.1. Efficiency for heavy metal removal in the batch method

3.1.1.Sulfonated polystyrene resin (SPS)

The efficiency of the SPS resin was determined by measuring the concentration of the unabsorbed heavy metal ions present in the filtrate solutions of the metal ions separately. The results obtained are shown in Table 1 and Figure 2. It was found that Pb^{2+} has a low efficiency (7%) at pH 6 (46.34 mg L^{-1}) and high efficiency (33%) at pH 8 (16.73 mg L^{-1}). While cadmium ion has a low efficiency (٪٧٣) at pH ١٣٫٥١) ٤ mg L^{-1}) and high efficiency (77%) at pH 8 (11.7 mg L^{-1}), and Fe^{3+} has the highest efficiencies slightly above (٪٩٨) at all pH values. This positively reflected the ability of the three prepared resins to work as ion exchange resins for heavy metal removal with high efficiency even with a low initial concentration. Using sulfonated polystyrene resin to separate Zn^{2+}, Cu^{2+}, and Cd^{2+} heavy metal ions from their solutions, Tran and his coworkers came to the same conclusion [6].

Table 1. The efficiency of SPS resin in a batch method towards different heavy metal ions at different pH (Unit: mg L^{-1})

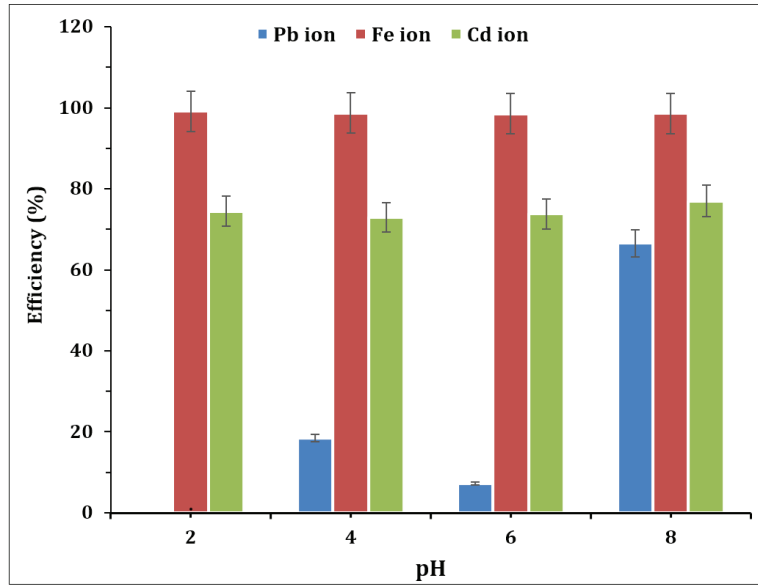| pH	Pb	%Efficiency Pb	Fe	%Efficiency Fe	Cd	%Efficiency Cd
2	50.00	0.00	0.41	99.18	12.77	74.46
4	40.76	18.48	0.64	98.72	13.51	73.00
6	46.34	7.32	0.72	98.56	13.11	73.80
8	16.73	66.54	0.70	98.60	11.70	77.00

Fig. 2. The efficiency of SPS resin towards various metal ions at different pH in a batch method.

Table 2. Efficacy of SPS-g-Acryl in a batch method resin towards different metal ions at different pH (Unit: mg L^{-1})

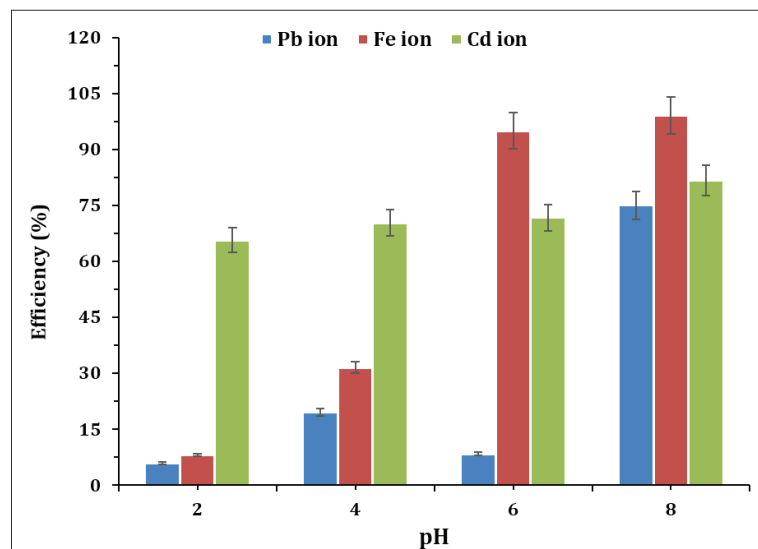| pH	Pb	Efficiency Pb%	Fe	Efficiency Fe%	Cd	Efficiency Cd%
2	47.03	5.94	45.96	8.10	17.18	65.64
4	40.23	19.54	34.25	31.50	14.87	70.30
6	45.80	8.40	2.60	95.00	14.16	71.70
8	12.53	75.00	0.52	99.00	9.47	81.70

Fig. 3. The efficiency of SPS-g-Acryl resin towards various metal ions at different pH using the batch method

3.1.2.Sulfonate polystyrene-g-acrylamide (SPS-g-Acryl)

It is widely understood that most polymers used in water and wastewater treatment are acrylamide-based. The basic acrylamide monomer may be combined to provide polymers of varying iconicity. Though related, these exhibit somewhat different properties based on their monomer characteristics and how the copolymerization reaction takes place. SPS-g-acrylamide for water treatment due to its high cationic charge content. This polymer is primarily nonionic at pH <4, but deprotonation to the cationic form (SPS-g-Acryl) occurs at increasing pH (8) [26]. The effect of different pH values, which are 2, 4, 6, and 8, respectively, was studied for removing three heavy metal ions by SPS-g-Acryl resin, and the results are shown in Table 2 and Figure 3. It is noted that the Pb^{2+} ion had a low efficiency (5.94%) at pH 2 (47.03 mg L^{-1}) and high efficiency (75%) at pH 8 (12.53 mg L^{-1}). On the other hand, for Cd^{2+}, efficiency is low (65.64%) at pH 2 (17.18 mg L^{-1}) and high (81.70%) at pH 8 (9.47 mg L^{-1}). While for Fe^{3+}, lower efficiency (8.1%) was obtained at pH 2 (45.96 mg L^{-1}) and high efficiency (99%) at pH 8 (0.52 mg L^{-1}).

3.1.3.Sulfonated polystyrene-grafted-chitosan (SPS-g-Chit)

Sulfonated polystyrene is a polymerized styrene monomer by the sulfonation process. This process produces a grafted polymer with improved properties

of this material and increases the crosslinking process, which leads to the expansion of the polymeric network [27.28]. When chitosan is grafted onto this network, it will lead to better properties due to the high functionality of the chitosan polymer, in addition to relying on the active groups whose work was previously mentioned and how their efficiency increases with increasing pH [29,30]. The effect of different pH values (2, 4, 6, and 8) was also investigated, and the results are shown in Table 3 and Figure 4. Pb^{2+} ions had a low efficiency (45.38%) at pH 2 (27.31 mg L^{-1}) and a high efficiency (85%) at pH 8 (7.5 mg L^{-1}). Whereas, Cd^{2+} and Fe^{3+} ions presented the highest efficiencies at all pH values, slightly higher than 99% (Table 3).

3.2. Treatment of single heavy metal ions by column method

Chromatography is a physical method of analysis and separation that uses a stationary phase with a large surface area and a mobile phase that flows through and generally contains the sample. The ion exchange column belongs to the (solid-liquid) chromatography category. When a mixture of two or more ions runs through the column in quantities that are minor compared to the column's total exchange capacity. It was completely absorbed by the resin and then separated from its constituents using an appropriate effluent to elute out the weakly bound ionic resin first, then the second ion, and so on. Elution is the process of separating these ions

Table 3. The efficiency of SPS-g-Chit in a batch method resin towards different metal ions at different pH (Unit: mg L^{-1})

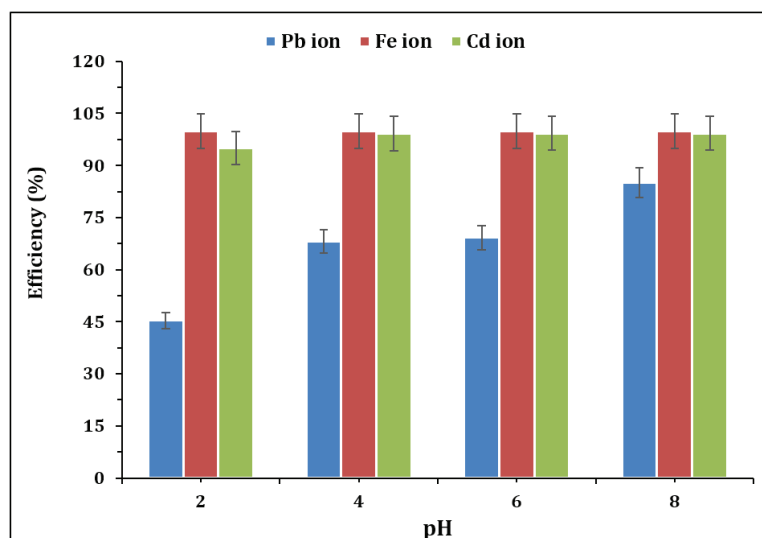| pH	Pb	%Efficiency Pb	Fe	%Efficiency Fe	Cd	%Efficiency Cd
2	27.31	45.38	0.02	99.96	2.53	95.00
4	15.96	68.08	0.003	99.99	0.37	99.26
6	15.38	69.24	0.01	99.98	0.35	99.30
8	7.50	85.00	0.01	99.98	0.35	99.30

Fig. 4. The efficiency of SPS-g-Chit resin
in a batch method towards various metal ions at different pH

until they are separated quantitatively. The Flame atomic absorption spectrometer method is. The optimum pH of 8 is favorable due to the partial hydrolysis of metal ions. As previously stated, the best efficiency result in pH obtained from the batch method revealed that the SPS-g-Chit resin was the most effective at ion exchange toward the three metal ions studied. Therefore, it was used for the removal of single metal ions by the column method. The pH 8 for the SPS-g-Chit resin is an exchange efficiency of 98.51% for Pb^{2+} and 99.76% for Cd^{2+}, whereas the exchange effectiveness of Fe^{3+} is reduced to 78.36%.

3.3. Treatment of heavy metal ions mixture
Table 4 shows that the efficiency of the SPS-Chit resin showed a high exchange efficiency for

Pb^{3+} and Cd^{2+}. The grafting process of SPS with chitosan added another active group to increase the ion exchange efficiency of the SPS. The chitosan is characterized by its great affinity with metal ions due to its high content of amine groups in a rational manner, where the exchange mechanism depends on each of the protons of these amine groups or metal ions, as well as cross-linking, which tends to enlarge the polymeric network, resulting in better efficiency [31]. This was also confirmed in our previous studies; adsorption capacities were higher when the active group concentration increased [8,10,11]. The resin presented no exchange effectiveness for Fe^{3+}. This may be due to the ferric ions' ionic size differing from the ionic volume of lead and cadmium; these ions will compete for the exchange.

Table 4. The efficiency of SPS-g-Chit resin in a column method towards different metal ions
at other times (Unit: mg L^{-1})

Time (min)	Pb	%Efficiency Pb	Fe	%Efficiency Fe	Cd	%Efficiency Cd
30	0.417	98.00	16.6	0	0.733	95.00
60	0	100	16.6	0	0.05	99.60
90	0	100	16.6	0	0.037	99.70
120	0	100	16.6	0	0.022	99.80
150	0	100	16.6	0	0.01	99.90

Table 5. Regeneration of the SPS-g-Chit resin

Metal Ion	Conc. (mg L^{-1})	Regeneration Efficiency(%)
Pb	0.14	99.72
Cd	0.10	99.81
Fe	7.85	84.31

3.4. Regeneration of Loaded Resins

The SPS-g-Chit resin was selected for the ion exchange regeneration resin experiment because it has the greatest changeability toward the three metal ions used in this study (Pb^{2+}, Cd^{2+}, and Fe^{3+}). Table 5 shows the outcomes that were attained. It demonstrates that after around an hour of treatment, the lead and cadmium ions showed the maximum percentage of regenerating efficiency, confirming their robust specifications regarding loading capacity and the ability to use the SPS-g-Chit resin as an ion exchanger in industrial processes.

4. Conclusion

Recycling single-use teacups and shrimp cortex chitosan as ion exchange materials limits the extraction of natural resources and reduces environmental pollution. Ion exchange resins can be produced and used with less expense using alternative materials; one such material is polystyrene waste that has been sulfonated, and its grafted acrylamide monomer and chitosan polymer derivatives have the potential to have a higher ion exchange capacity. H+s competing with metal ions at lower pH levels were discovered to be responsible for better results in treating metal ions at higher pH levels of 8. In terms of their active groups, chemical structures, and stereotypical structures, the produced resins varied in performance depending on the metal ion and resin type used. In conclusion, as the raw material used to create ion exchange resin is made from waste materials, sulfonated polystyrene and using chitosan originally extracted from shrimp cortex are thought to be technically and environmentally possible to remove heavy metals at a reasonable cost.

5. Acknowledgements

6. References

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