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# Removal of Heavy Metals from Their Solution Using Polystyrene Adsorbent (Foil Take-Away Disposable Plates)

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**Abstract:** The presence of heavy metal ions, viz. Cr(vi), Mn(ii) and Cu(ii), in aquatic systems pose heavy risks to human health. Therefore, removal of such metal ions from water bodies may be considered an interesting and important research activity. This is a research work on the removal of heavy metals from their solution with the use of polystyrene. Polystyrene (Foil take-away disposable plates) was sourced locally. The Plates were ground to fine particles to increase the surface area for adsorption and then serial dilution was performed. The adsorption isotherm models used were Langmuir, Freundlich and Dubinin-Radushkevich (DR). The result from the models showed that Langmuir fits better for Cr(vi) and Cu(ii) while DR fits in better for Mn(ii). Results obtained showed that adsorption followed second order kinetics. Equilibrium was obtained at 30 minutes. Thermodynamic data for enthalpy ( $\Delta H$ ) for Cr, Cu, and Mn are 2036.986 J/mol, 24276.88 J/mol and 27469 J/mol respectively and showed that adsorption was found to be endothermic. Entropy results were -49.21888 J/K, -117.97566 J/K and 66.7828 J/K for Cr(vi), Cu(ii) and Mn(ii) respectively, showing a decrease in entropy. Free energy change showed that adsorption for Chromium and Manganese at temperatures 323, 343 and 363K were spontaneous, while Copper was non spontaneous. pH result showed maximum adsorption at pH of 6. This study showed that polystyrene fits better for the adsorption of Chromium and Copper ion in the Langmuir Isotherm model. While that of Manganese was described better by the Dubinin-Radushkevich Isotherm Model. It is hereby recommended that polystyrene wastes are good adsorbents for the removal of heavy metals from aqueous solutions. Therefore, should be employed for the removal of heavy metals in the environment, as it can be easily gotten even at a low cost.

**Keywords:** Heavy Metals, Isotherms, Langmuir, Freundlich, Dubinin-Radushkevich, Entropy, Thermodynamics, Free Energy

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## 1. Introduction

Drinking water obtained from springs may be contaminated by various toxic metals. One of the most important problems is the accumulation of toxic metals in food structures. The contaminated food can cause poisoning in humans and animals. Although some heavy metals are necessary for the growth of plants, after certain concentrations heavy metals become poisonous for both plants and heavy metal micro-organisms. Another important risk concerning contamination is the accumulation of these substances in the soil in the long term. Heavy metals are held in soil as a result of adsorption, chemical reaction and ion exchange of soil [1, 2].

Problems of the ecosystem are increasing with developing

technology. Heavy metal pollution is one of the main problems. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's waters may contain various toxic metals [3, 4].

Heavy metals have an effect on the enzymes. It has been determined that various metal ions hinder various enzymes responsible for mineralization of organic compounds in the earth. Therefore, studies on the removal of heavy metal pollution are increasing [5].

Styrene is obtained by reacting ethylene with benzene in the presence of Aluminum chloride to yield Ethylbenzene. The benzene group in this compound is then dehydrogenated

to yield phenylethylene, or styrene, a clear liquid hydrocarbon with the chemical structure  $\text{CH}_2=\text{CHC}_6\text{H}_5$ . Styrene is polymerized by using free-radical initiators primarily in bulk and suspension processes, although solution and emulsion methods are also employed.

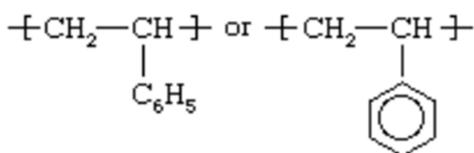


Figure 1. A structure of Polystyrene.

The structure of the polymer unit is shown above. The presence of the pendant phenyl ( $\text{C}_6\text{H}_5$ ) groups is key to the properties of polystyrene. Solid polystyrene is transparent, owing to these large, ring-shaped molecular groups, which prevent the polymer chains from packing into close, crystalline arrangements. In addition, the phenyl rings restrict rotation of the chains around the carbon-carbon bonds, lending the polymer its noted rigidity [5].

The polymerization of styrene has been known since 1839, when German pharmacist Eduard Simon reported its conversion into a solid later named metastyrol. As late as 1930, little commercial use had been found for the polymer, because of brittleness and crazing (minute cracking), which were caused by impurities that brought about the cross-linking of the polymer chains. By 1937 American chemist Robert Dreisbach and others at the Dow Chemical Company's physics laboratory had obtained purified styrene monomer through the dehydrogenation of ethylbenzene and developed a pilot polymerization process. By 1938 polystyrene was being produced commercially. It quickly became one of the most important modern plastics, owing to the low cost of producing large volumes of styrene monomer, the ease of shaping the melted polymer in injection-molding operations, and the optical and physical properties of the material [5].

Polystyrene foam was formerly made with the aid of chlorofluorCarbon blowing agents—a class of compounds that has been banned for environmental reasons. Now foamed by pentane or carbon dioxide gas, polystyrene is made into insulation and packaging materials as well as food containers such as beverage cups, egg cartons, and disposable plates and trays. Solid polystyrene products include injection-molded eating utensils, video-cassettes and audio-cassettes, and cases for audio-cassettes and compact discs. Many fresh foods are packaged in clear vacuum-formed polystyrene trays, owing to the high gas permeability and good water-vapour transmission of the material [5]. Despite its advantageous properties, polystyrene is brittle and flammable; it also softens in boiling water and, without the addition of chemical stabilizers, yellows upon prolonged exposure to sunlight. In order to reduce brittleness and improve impact strength, more than half of all polystyrene produced is blended with 5 to 10 percent butadiene rubber. This blend, suitable for toys and appliance parts, is marketed

as high-impact polystyrene (HIPS) [5].

Polystyrene is a vinyl polymer, one of the thermoplastic resins. Structurally, it is a long hydrocarbon chain, with a phenyl group attached to every other carbon atom [6]. Polystyrene is produced by free radical polymerization, from the monomer Phenylethene, a compound commonly known as styrene [7].

Amongst all the other methods used in the removal of the heavy metals, adsorption had been reported as an efficient and economic option, especially when the source of adsorbent is economical. Synthetic polymers like polyethylene, Nylon 6.6, polymethylmethacrylates and their derivatives have been found useful in different areas of life. They can be converted into useful materials as parachutes, etc. when these materials are immersed in solution such as sulphuric acid in order to attach sulphonic group to the polymer chain, these groups are responsible for the properties of the modified plastic. This makes them good adsorbent in removal of toxic metals in our environment [8]. Polystyrene used in packaging of electronics of all kinds are easily seen in the urban cities and even in towns. They have contributed heavily to the pollution of our environments. The indiscriminate dumping of these waste has led to the obstruction of our drainage systems denaturing, the environment. Therefore a way of collecting, pressing and recycling of these wastes to useful materials is urgently needed. Wastes effluents from industrial and mining areas containing heavy metal ions pose a threat to humans and even aquatic life. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy level etc. Toxicity can result in significant illness and reduced quality of life [9].

There is need to therefore, reduce the level of these heavy metal ions from waste effluents before they are discharged into the environment. It is well known that the increment in the world population as well as the use of amenities with various technologies which gave rise to need of more production of required things is responsible for increased pollution by various pollutants. Amongst the various pollutants, pollution due to heavy metals are getting increased due to enhanced applications of these metals. The experimental studies on adsorption by using resins and the electrodes surface of metals, such as Pt, Au and Si had been reported [10].

Safe handling, treatment and disposal of effluents containing heavy metals are of great concern from the perspective of both health and environment. Heavy metals pose serious threat to public health because of their non-biodegradable and persistent nature. They are carcinogenic even at very low concentrations. Major sources of heavy metal pollution are mining, welding, alloy manufacturing, tannery, jewelry, chemicals, fuel, ammunition and metallurgical, electrical and electronic goods producing industries in developed as well as developing countries [11].

A variety of conventional and modern methods have been devised for the effective removal of heavy metals from contaminated water. The most common are chemical precipitation, oxidation-reduction, electrochemical treatment,

evaporative recovery, filtration, ion-exchange, solvent extraction, ultra filtration, reverse osmosis, electro dialysis, adsorption and membrane technologies [12]. However, most of these processes suffer from one drawback or the other, especially when the metals in solution are in the range of 1-100 mgL<sup>-1</sup>. For instance, precipitation methods are comparably simple and reliable but require high installation cost for setting large tanks for the effective precipitation [13].

Moreover, there is a further need to treat the effluent in order to ensure that the treated water contains the impurities below the permissible limit. Recently, adsorption technology has emerged as a powerful economical, simple and effective tool for the removal of heavy metal ions from wastewater. Of all the known heavy metal ions, lead is a potential threat from the environmental point of view as, the metal is widely used in a variety of occasions particularly in lead smelting, battery manufacturing, paper and pulp industry and most importantly in dentistry [14].

Removal of Cu (II) from aqueous solution by different adsorbents such as shells of lentil (LS), wheat (WS) and rice (RS) was investigated. The maximum sorption capacities for Cu(II) on LS, WS and RS adsorbents at 293K, 313K, 333 K were found to be 8.977mg/g, 9.510mg/g and 9.588mg/g; 7.391mg/g, 16.077mg/g and 17.422mg/g; 1.854mg/g, 2.314mg/g and 2.954 mg/g, respectively. The sorption of Cd (II) from aqueous solution by rice husk, a surplus agricultural byproduct has been investigated [15].

Some simple and low-cost chemical modifications resulted in increasing of the sorption capacity of raw rice husk (RRH) from 8.58mg/g to 11.12mg/g, 20.24mg/g, 16.18 mg/g and reducing the equilibrium time from 10 h of RRH to 2, 4 and 1 h for epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH), sodium bicarbonate treated rice husk (NCRH), respectively [16]. Conrad did research on sorption of Zn(II) and Pb(II) on coir, and found that Pb(II) had a higher sorption affinity than Zn(II). In the review, an extensive list of plant wastes as adsorbents including rice husks, spent grain, sawdust, sugarcane bagasse, fruit wastes, weeds and others were compiled [16].

Some of the treated adsorbents showed good sorption capacities for Cd, Cu, Pb, Zn and Ni. The interactions of metal ions with chitosan-based adsorbents were reviewed by [17], and they concluded that metal ions can be adsorbed by chelation on amine groups of chitosan in near neutral solutions. These interactions of metal ions with chitosan can be used for decontamination of effluents, for the recovery of valuable metal ions but also for the development of new materials or new processes involving metal-loaded chitosan [18, 19]. Miretzky reviewed the recent developments in Hg(II) removal in wastewater treatment, using chitosan and its derivatives in order to provide useful information about the different technologies and reported the sorption capacity of chitosan and chitosan derivatives under different experimental conditions. Chelating polymer resins are found to be more selective by nature as compared to other conventional techniques in the removal of metal ions. In the light of the above, several polystyrene-supported chelating

polymer resins have been synthesized recently. In continuation, we report here the metal ion uptake properties of these resins [19].

The work focuses on the use of a synthetic polymer (polystyrene) to remove heavy metal from their solution. Polystyrene is a hard, stiff, brilliantly transparent synthetic resin produced by the polymerization of styrene. It is widely employed in the food-service industry as rigid trays and containers, disposable eating utensils, and foamed cups, plates, and bowls. Polystyrene is also copolymerized, or blended with other polymers, lending hardness and rigidity to a number of important plastic and rubber products.

## 2. Method

### 2.1. Materials

#### 2.1.1. Apparatus

The apparatus used include; Conical flasks, Mortar and Pestle, Beakers, Stirrer, Stop watch, Spatula, Measuring cylinder, Filter, papers, Weighing balance [Labtech model], Sample bottles, Atomic Absorption Spectrophotometer (AAS) [Agilent FS model] and Thermostat water bath [DK 424 technad U.S.A model].

#### 2.1.2. Reagents

Distilled water, Chloroform, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> salt, KMnO<sub>4</sub> salt, CuSO<sub>4</sub>.5H<sub>2</sub>O salt. All the chemicals used, were of analytical grade. And all the glass ware were washed and dried before and after each experiment.

### 2.2. Adsorbent and Adsorbate Preparation

The Polystyrene (Foil take-away disposable plates) was sourced locally. The Plates were ground to fine particles to increase the surface area for adsorption. The polystyrene was of uniform length and 3g of the polystyrene was weighed and used in each experiment.

### 2.3. Preparation of Stock Solution

Stock solution containing 1000ppm of ions of chromium was prepared by dissolving 2.9g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 100ml distilled water and then making it up to 1000ml. 10 ml of the Cr solution was then withdrawn from the stock solution and made up to 1000ml which gave 10ppm concentration.

Stock solution containing 1000ppm of ions of manganese (II) was prepared, by dissolving 3.07g of MnSO<sub>4</sub>.H<sub>2</sub>O in 100ml distilled water and then it was made up to 1000ml.

Stock solution containing 1000ppm of ions of copper(II) was prepared, by dissolving 3.929g of CuSO<sub>4</sub>.5H<sub>2</sub>O in 100ml distilled water and then it was made up to 1000ml.

Various concentrations that were used in this experiment were prepared by serial dilutions from the stock solutions.

#### *Serial Dilution of the stock solution*

To prepare 10ppm: 10ml was pipetted out from the stock solution and put into a litre volumetric flask. The volume was made up to the mark with de-ionized water. The same procedure was applied in the preparation of 20ppm, 30ppm,

40ppm and 50ppm.

**2.4. Procedures Used for the Adsorption of the Metal Ions from Solution Using Polystyrene**

**2.4.1. Equilibrium Studies**

3g of the adsorbent was weighed into different beakers, each containing 50ml of varying concentration of 10, 20, 30, 40 and 50ppm of  $MnSO_4 \cdot H_2O$ ,  $CuSO_4 \cdot 5H_2O$  and  $K_2Cr_2O_7$  solution respectively. The mixture was stirred thoroughly with a stirrer and then allowed to stand for 1hour, after which 10ml was drawn out from each solution and filtered. The filtrate was analyzed using an AAS machine.

**2.4.2. Kinetics Study Experiment**

40ppm solution of  $MnSO_4 \cdot H_2O$ ,  $K_2Cr_2O_7$  and  $CuSO_4 \cdot 5H_2O$  were prepared and 100ml was withdrawn and put into three different beakers. 3g of the adsorbent was added to each of the beakers respectively. The mixture were stirred and allowed to stand for time intervals of 5, 10, 30, 60, 90, and 120mins, while other parameters were kept constant. 10ml was drawn from the solution and filtered. The filtrate was then analyzed for metal ion concentration and the results obtained were used for the kinetic study.

**2.4.3. Thermodynamics Study Experiment**

Adsorption of Cr(vi), Cu(ii) and Mn(ii) ion from their aqueous solution were investigated over the temperature range of 50C, 70C and 90C. 40ml of  $CuSO_4 \cdot 5H_2O$ ,  $K_2Cr_2O_7$  and  $MnSO_4 \cdot H_2O$  was drawn respectively from the stock solution. This was made up to 1000ml to produce 40mg/l of Cu(ii), Cr(vi) and Mn(ii) respectively. 100ml of the prepared solution was put into three different beakers respectively. 3g of the adsorbent was added to each beaker and the mixtures were stirred for even distribution. These beakers were placed in a thermostat water bath set at temperature of 50C. The beakers were allowed to stand in the bath for an hour and after which the samples were drawn from them and filtered for analysis. These were repeated for temperatures of 70C and 90C.

**2.4.4. PH Experiment**

The uptake of heavy metal as a function of  $H^+$  ion concentration was determined in the pH range of 2-8. The adjustment of the pH solution was carried out by adding required amount of conc.  $H_2SO_4$  and NaOH.

**3. Results**

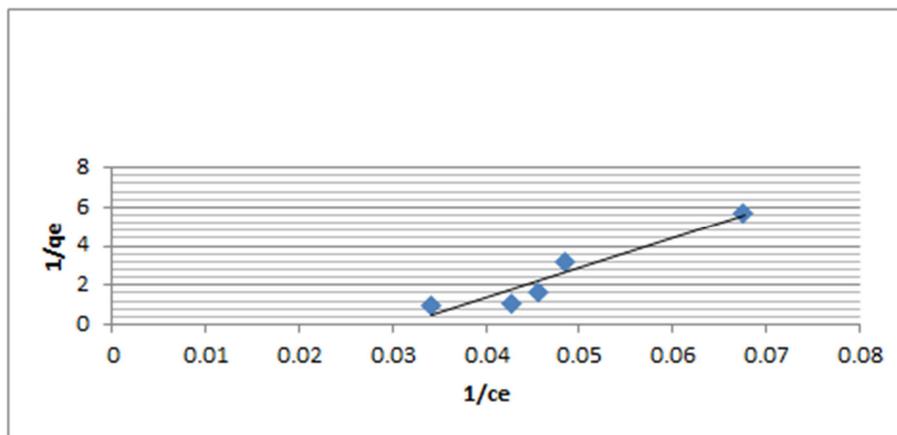


Figure 2. Langmuir Isotherm plot for Chromium ion adsorption.

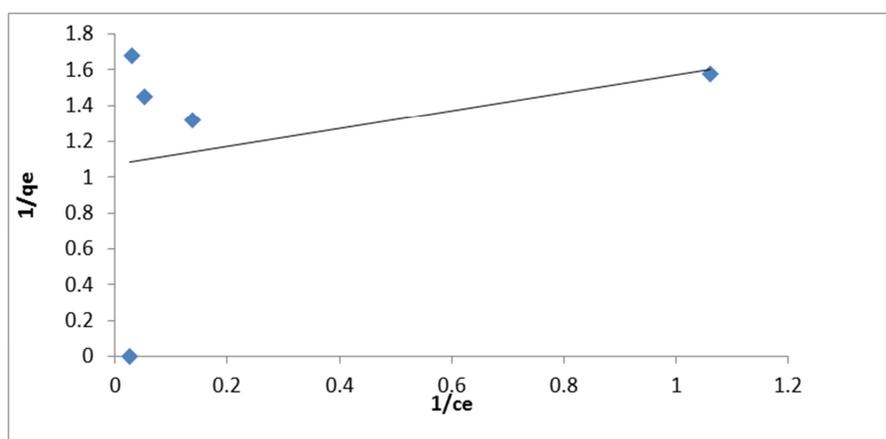


Figure 3. Langmuir Isotherm for Copper ion adsorption.

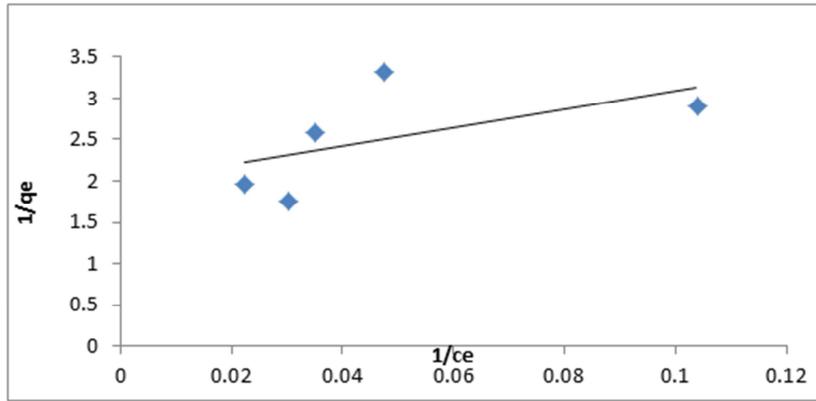


Figure 4. Langmuir Isotherm for Manganese ion adsorption.

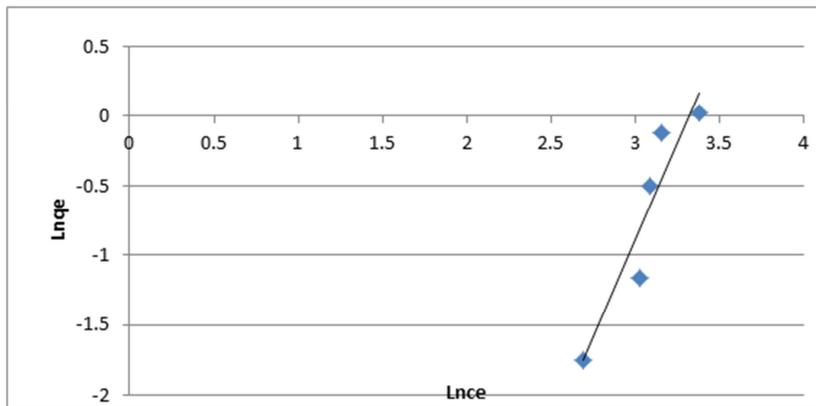


Figure 5. Freundlich Isotherm plot for chromium ion adsorption.

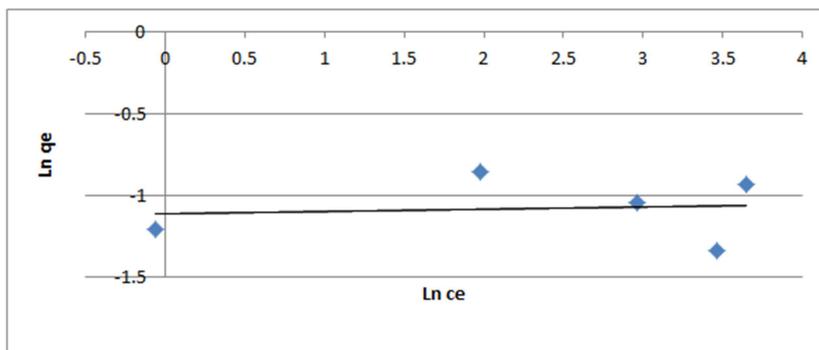


Figure 6. Freundlich Isotherm plot for adsorption of copper ion.

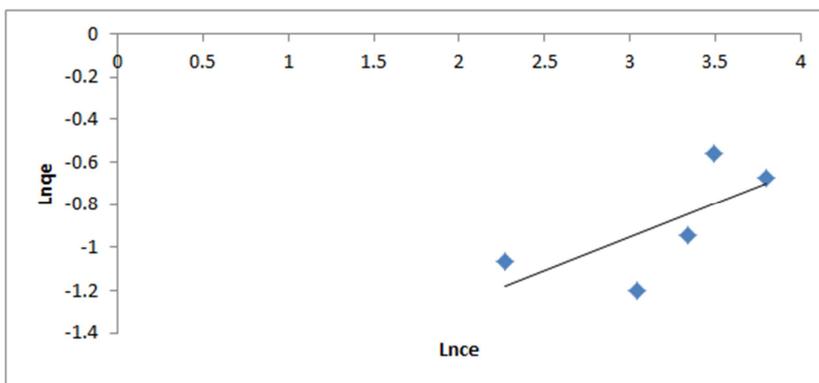


Figure 7. Freundlich Isotherm for adsorption of Manganese ion.

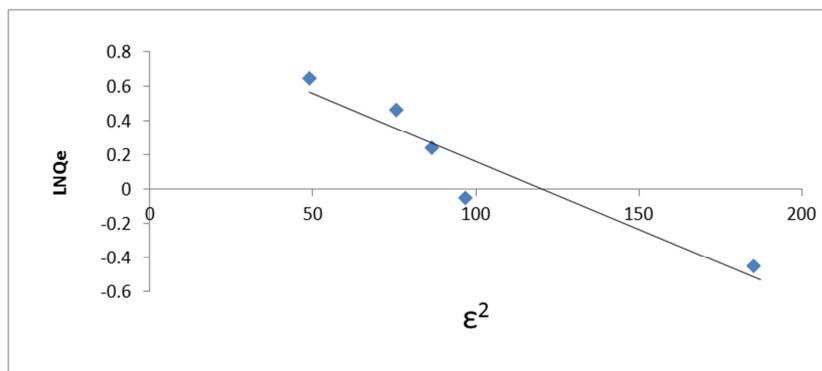


Figure 8. Dubinin-Radushkevich Isotherm plot for Chromium ion.

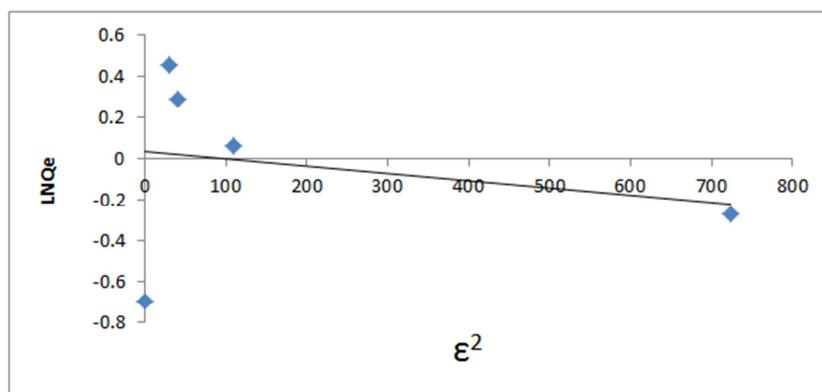


Figure 9. Dubinin-Radushkevich Isotherm plot for Copper ion adsorption.

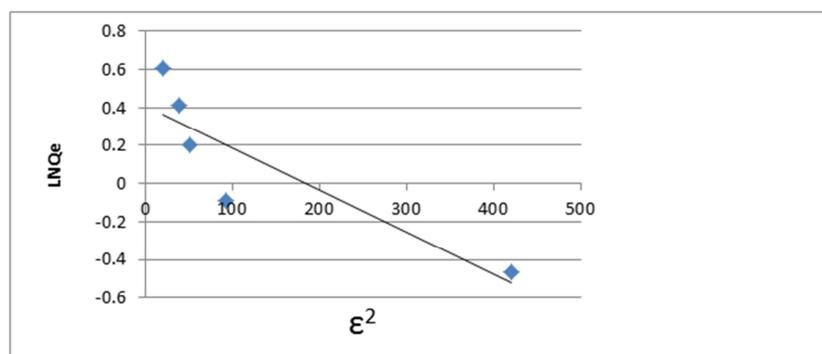


Figure 10. Dubinin-Radushkevich Isotherm for Manganese ion adsorption.

Table 1. Isotherm parameters for Cr, Cu and Mn.

Metal	Isotherm Parameter for Adsorption								
	Isotherm Model	Slope	Intercept	R <sup>2</sup>	Q <sub>m</sub>	n	LnK <sub>T</sub> , LnK <sub>F</sub>	K <sub>F</sub> , K <sub>L</sub> and K <sub>T</sub>	R <sub>L</sub>
Cr	Freundlich	2.815	-9.334	0.872	-0.206	0.355	-0.8879	-0.03	2.5
	Langmuir	154.6	-4.846	0.915					
	DR	-0.007	0.95	0.893					
Cu	Freundlich	0.013	-1.104	0.01	0.93	7.9	-0.8879	2.17	0.044
	Langmuir	0.499	1.074	0.106					
	DR	0	0.032	0.055					
Mn	Freundlich	0.312	-1.886	0.473	0.51	3.21	-0.8879	5.605	0.00884
	Langmuir	11.21	1.966	0.318					
	DR	-0.002	0.41	0.768					

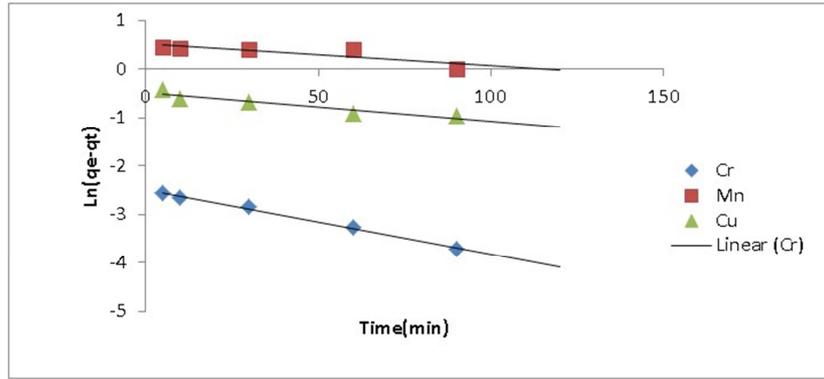


Figure 11. Pseudo 1st order plot for adsorption of Cr, Mn and Cu ion.

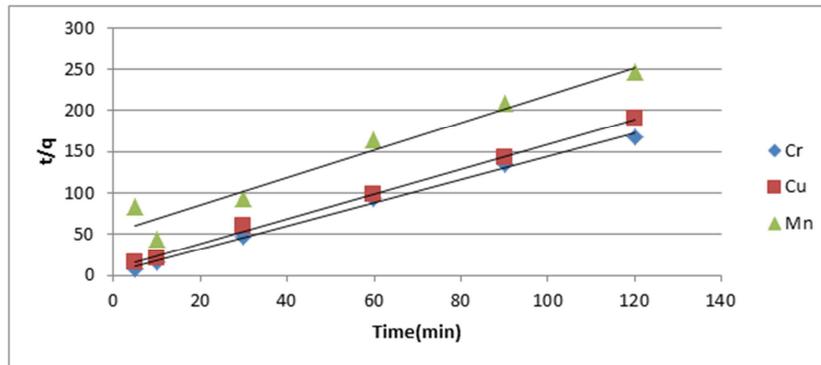


Figure 12. Pseudo 2nd Order plot for adsorption of Cr, Cu and Mn ions.

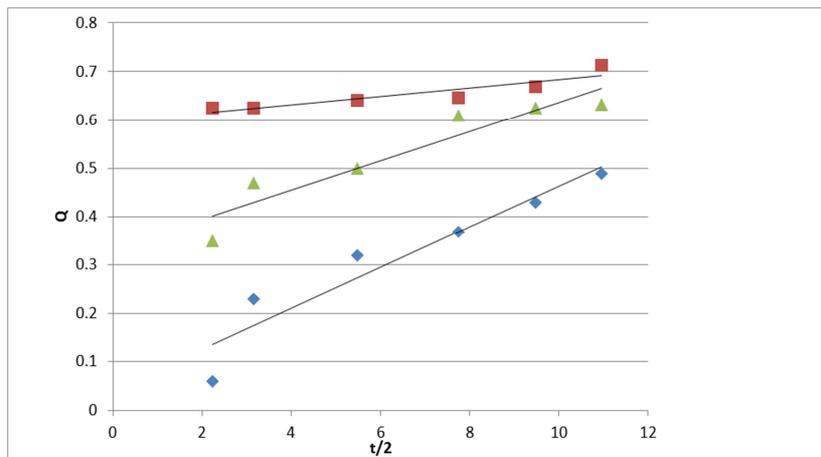


Figure 13. Weber Morris plot for adsorption of Mn, Cr and Cu ion.

Table 2. Kinetic parameters for Cr, Cu and Mn.

Metal	Model	Slope	Intercept	R <sup>2</sup>	Qe(theoretical)	Qe(experimental)	K <sub>ad</sub>	h
Cr	Lagergren	-0.013	-2.48	0.993	0.083743	0.9667	0.013	
	Pseudo-second	1.415	3.388	0.996	0.706714	0.9667	0.590976	0.295159
	WM	0.008	0.597	0.828				
Cu	Lagergren	-0.005	-0.482	0.878	0.617547	0.9667	0.005	
	Pseudo-second	1.51	8.66	0.998	0.662252	0.9667	0.263291	0.115473
	WM	0.030	0.331	0.887				
Mn	Lagergren	0.004	0.516	0.692	1.675313	0.9667	-0.004	
	Pseudo-second	1.666	52.66	0.950		0.9667	0.827275	0.202143
	WM	0.042	0.041	0.904				

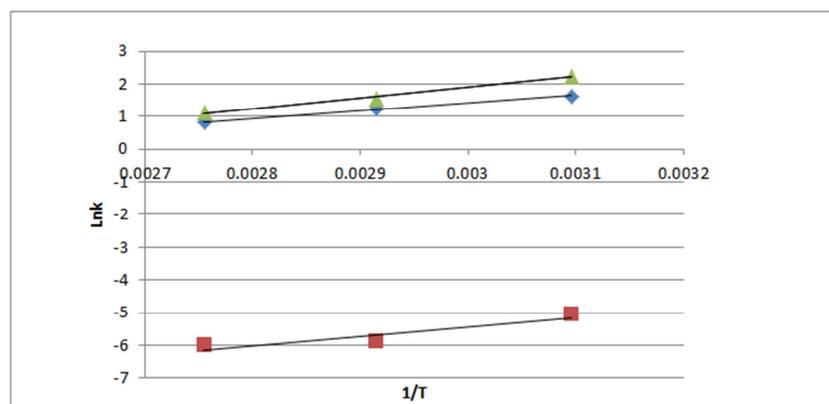


Figure 14. Thermodynamic plot for Mn, Cr and Cu ion.

Table 3. Thermodynamic Parameter for Cr, Cu and Mn.

Metal	Slope	Intercept	$\Delta H(\text{J/mol})$	$\Delta S$	Temperature (K)	$\Delta G$				
						$\Delta G$	$\Delta G$	$\Delta G$		
Cr	2449	-5.92	20360.99	-49.2189	323	343	363	-4438.28	-355.21	-2461.92
Cu	2920	-14.19	24276.88	-117.976	323	343	363	13555.1	16841.09	18198.08
Mn	3304	-8.02	27469.46	-66.6783	323	343	363	-6027.17	-4395.58	-3385.75

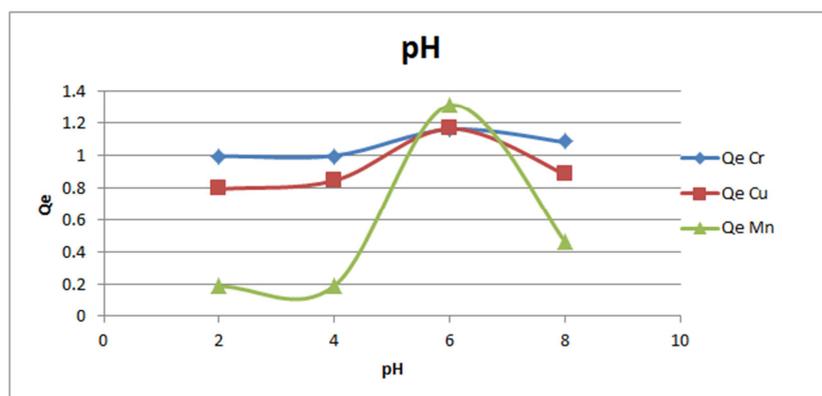


Figure 15. A plot of pH for adsorption of Cr, Cu and Mn ion.

## 4. Discussion

### Adsorption Isotherm

Considering the Isotherm models for chromium,  $R^2$  values obtained from the Langmuir model for Cr is closer to 1, and therefore fits better for the adsorption of chromium ion.

Looking at the figure(s) 2, 3, 4, 5, 6, 7, 8, 9 and 10 for the three isotherm models. For copper it can be seen that the Langmuir fits better for the study because it has a higher  $R^2$  value compared to the two other models.

Considering that of Manganese, the Dubinin-Radushkevich isotherm model fits in better for the study of this metal ion adsorption study, this is because it has the highest  $R^2$  value. This can be seen from table 1.

### Kinetics

Comparing the three methods, it can be seen that the pseudo 2<sup>nd</sup> order has the highest value of  $R^2$  close to 1. Hence, it better describes the adsorption of the three metal ions unlike the other two methods (1<sup>st</sup> order and Weber

Morris).

Also, looking at the  $K_{ad}$  value for the 1<sup>st</sup> order and 2<sup>nd</sup> order in table 2, it can be seen that the 2<sup>nd</sup> order had the highest value. This indicates that the 2<sup>nd</sup> order describes better the adsorption of these metals.

### Thermodynamic studies

The variation in the extent of adsorption with respect to temperature has been explained based on the thermodynamic parameters viz; Free energy, entropy and enthalpy change.

$\Delta H$  for chromium, copper and manganese: Polystyrene had a positive value of  $\Delta H$  as 20360.986, 24276.88 and 27469.406 J/mol/K for Cr, Cu and Mn respectively. This indicates that the reaction is endothermic.

$\Delta S$  for chromium, copper and manganese: comparing the entropy change of the three metal ions, it showed that Cr (VI) has -49.21888, Cu -117.97566 and Mn(ii) has -66.7828. They all have a negative entropy change, hence it indicates that there is a decrease in randomness at the solid-liquid interface, the degree of randomness is higher in Cr(vi) since it is the most positive.

$\Delta G$  for chromium: The overall free energy change for chromium during the adsorption are all negative, at temperatures 323, 343 and 363 and the values are -4438.28, -3554.21 and 2461.92 respectively, hence it is spontaneous.

$\Delta G$  for copper: The overall free energy change for copper are all positive at different temperatures of 323, 343 and 363 and the values are 13555.1, 16841.09 and 18198.08 J/mol. Hence, it is not a spontaneous reaction.

$\Delta G$  for Manganese: The overall free energy change for Manganese are all negative and, the values are -6027.17, -4395.58 and -3385.75 J/mol. Hence, it is spontaneous.

Effect of pH on uptake of the metal ions

From Figure 15 above, adsorption was less at a lower pH and increases at a higher pH but reaches a maximum level at a pH of 6 and later declines to a pH of 8. At a lower pH values (< pH 4), protonation of chelating groups takes place, complexation with available ligands is reduced and hence the percentage uptake decreases. At a higher pH values (> PH 4), deprotonation takes place and hence the percentage uptake increases through the formation of stable polymer-metal complexes. The uptake of Mn(ii) and Cu(ii) increases with an increase in pH and reaches a plateau value at a pH of 6. In the case of Cr(vi), the plateau value is also observed at a pH 6.

This is believed to be as a result of the metal ions being positively charged. Therefore, at lower pH, the  $H^+$  being lighter than the ions namely; Cr(vi), Mn(ii) and Cu(ii), would preferentially occupy the active site for adsorption. At a higher pH there happens to be a decline.

## 5. Conclusions

The presence of heavy metal ions, viz;Cr(vi), Mn(ii) and Cu(ii), in aquatic systems pose heavy risks to human health. Therefore, removal of such metal ions from water bodies may be considered an interesting and important research activity. Polystyrene resins are stable, and can be used for the removal of metal ions at room temperature. Their metal uptake efficiency increases with pH and reaches a plateau at pH 6 for Mn(ii)Cu(ii) and Cr(vi).

This study showed that polystyrene can be used as a suitable adsorbent for the removal of these heavy metals (copper, Manganese and Chromium) ions from solutions. This research also showed that polystyrene fits better for the adsorption of chromium and copper ion in the Langmuir isotherm model. While that of Manganese was described better by the Dubinin-Radushkevich isotherm model.

From the above conclusions, it is hereby recommended that polystyrene wastes are good adsorbents for the removal of heavy metals from aqueous solutions. Therefore, should be employed for the removal of heavy metals in the environment, as it can be easily gotten even at a low cost.

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