

## **The use of new modified polymers matrixes for removal of some metal ion from aqueous solution**

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**Summary:** In this study the removal of Zn, Ni and Ca ions investigated using new synthetic polymers which are sulfonated poly (vinyl phenol), poly (P-hydroxy styrene) and poly (4-vinyl co-methyl methacrylate). The adsorption of metals ions were carried out at different pH values of 2–9. It was shown that the amount of Zn ion removed from solution increases rapidly from pH 2 to pH 9. At pH 4, the removal efficiency of Zn ion was 49%, while at pH 9 was 71%. It was concluded that the amounts of Zn ion removed from solution varied from the highest value of 41 % at pH 8 to the lowest one of 20% at pH 4. The removal of Zn ion from solution occurs via exchange with hydroxyl function group linked to the polymer matrix of poly (p-hydroxy styrene). The effect of pH values on the exchange process indicated that the amounts of Ni metal ion adsorbed (Q) on poly (4-vinyl phenol co-methyl methacrylate) are ranged from 1.0 to 19.2 mole/g at pH values of 5.0 and 9.0 respectively. The optimum amount of Ca ion adsorbed (Q) on poly (4-vinyl phenol co-methyl methacrylate) is 9.5 mole/g at pH reading of 6.0 respectively. The correlation coefficient and other parameters obtained for the adsorbent are discussed, and indicated that the experimental data fitted well to Langmuir model.

### **Introduction**

The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life, beside the fact that these metals kill microorganisms during biological treatment of wastewater with a consequent water purification process delay<sup>(1)</sup>. In addition to, the presence of heavy metals in soil and industrial wastewater, can be an important source of pollution, and may be a severe health hazard. This is mainly due to their non-degradability and their toxicity <sup>(2)</sup> for instance, copper which considered in many studies, may lead to severe mucosal and a central nervous irritations, necrotic changes in the liver and kidney, etc., if an intake of excessively large doses. Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, <sup>(1)</sup> evaporative recovery, filtration, ion exchange, and membrane technologies have been widely used to remove heavy

metal ions from industrial wastewater. On the other hand, the treatment of effluent containing such heavy metals using adsorbents such as activated carbon, zeolites and organic polymers possess various advantages. Firstly, their pore structure can be finely tuned by the rigid node-strut topology, in particular by the average strut length<sup>(3)</sup>. Secondly, the surface can be functionalized by a wide variety of synthetic strategies, for example, moieties that could enhance binding affinities or monomers in molecular level. Thirdly, it is well known that most organic polymers are highly stable to air and water moisture. More importantly; some organic polymers can be synthesized reproducibly from well-defined monomers, although this is often challenging with activated carbon. They can also be easily woven into desired soft patterns, which is almost impossible for the hard adsorbents. These advantages render microporous polymer metal complexes have been of great interest because of their practical convenience and operational flexibility. Functionalized polymers have been used as carrier in various organic and inorganic synthetic transformations. When compared to various techniques that exist for the removal of metal ions from water such as solvent extraction and ion exchange techniques. The advantages of the use of Functionalized polymers as ion exchange resins over conventional ion exchangers include high metal to polymer bond energies and selective separation<sup>(4)</sup>.

Various techniques including chemical precipitation, extraction, adsorption electroflotation, flotation, ion exchange, reverse osmosis, electro dialysis, electrolysis, etc. can be used for removing the heavy metals contained in wastewaters<sup>(5)</sup>. The aim of the work is to study the sorption behavior of the synthesized polymers toward metals ions have been investigate in batch method where the factors which affect on removal of metals ions such as pH and doses of synthesized polymers will be studied. The interaction of metal ion and new polymers will be carried using I.R and elemental analysis techniques.

## Materials and methods

Poly (hydroxyl styrene) with MW  $100 \times 10^3$  was kindly supplied by triquest, LP (USA) as small beads. Poly (4-vinyl phenol co-methyl methacrylate) was purchased from Sigma-Aldrich, USA and was used as received; Sulfuric acid and fuming sulfuric acid were purchased from Aldrich and were used as received. Sulfonated poly (hydroxy styrene) was prepared according to the method described in the following experimental part.

### Synthesis of Sulfonated poly (hydroxy styrene)

Poly (hydroxy styrene) or known as Poly (vinyl phenol) was sulphonated according to the procedure <sup>(6)</sup> described as follows: The polymer (2 g) was transferred to a 50-ml flask, then 12 g fuming sulfuric acid (20%  $\text{SO}_3$ ) was added. The reaction mixture was stirred at room temperature for 12 h. The resulting sulfonated polymer (SPVP) was a violet gel. Deionized water was added to the product, which became a highly swollen gel with a deep violet color. The product was filtered and rigorously washed with distilled water to remove excess acid. The filtration was difficult as a result of the high swell ability of the product. The product was dried under vacuum at  $40^\circ\text{C}$  for one week <sup>(6)</sup>. The sulfonation level was determined by elemental analysis. The reaction scheme is outlined in Scheme 1.

Aqueous solutions containing Zn, Ni and Ca ions (0.01M) were prepared from nitrate salt (A.R grade) in double distilled water. The solution pH was adjusted by adding acid (acetic acid) and base (ammonium hydroxide) and measured using pH-meter (Oakton-47589, USA); the pH-meter was standardized using buffer solutions of pH values of 4.0, 7.0 and 10.0.

### Sorption measurements using batch method

In adsorption experiments (batch process), a fixed dry weight of polymer and 10 mL of an aqueous metal solution was placed in a 250 mL glass–stopper flask and shaken using a thermostatic shaker (Hanigsen/W-Germany, D 3165, Kotterman) for period (1hr) . The temperature was controlled at 298 K. After filtration, the equilibrium concentration of metal was analyzed using atomic absorption spectrometer ( Perkin–Elmer 2380, USA). Each run was duplicated under the identical conditions and the results of absorption of each metal were compared to those of

standard metal solution. The amount of metal removed (efficiency %) was obtained from the following equation (1)

$$\text{Efficiency \%} = [(C_o - C_e)/C_o] \times 100 \quad \text{Eq (1)}$$

Where  $C_o$  and  $C_e$  are the initial and the equilibrium liquid concentrations mole/L, respectively, while amount of adsorbed metal  $Q$  was given as the following:

$$Q = [(C_o - C_e) / W] \times V \quad \text{Eq (2)}$$

$V$  is the volume solution (L) and  $W$  is the amount of dry weight polymer used (g)<sup>(1)</sup>. To investigate the interaction between metal ion and polymers, I.R spectra were taken on KBr discs using FTIR spectrophotometer (Spectrum BX-Perkin Elmer, USA). Elemental analyses were carried out by Schwarzkopf Micro analytical Laboratory, INC, Laboratory, USA.

## Results and discussion

### Polymer modification:

Poly (vinyl phenol) PVP was modified with the aim of introducing sulfonic group functionality into the phenyl ring of the polymer. The introduction of the sulfonic group was tried with fuming sulfuric acid as described in the Experimental Part (Scheme1). The sulfonation of the PVP by this method was very efficient and yielded 91% sulfonation of the polymer as indicated from elemental analysis of 15% of sulfur content (Theoretical 16 %).

### Metal ion uptake using the selected polymers

#### Effect of pH on metal ion uptake

It is well known that the removal of heavy metals by adsorbent depends on the pH of the initial solution. Therefore, in order to establish the effect of pH on the adsorption of metals ions, the batch equilibrium studies were carried out in different pH values. The pH range was chosen as 2–9. Table 1 shows the amount of removal of Zinc ion using sulfonated poly (hydroxy styrene) from aqueous solution as a function of pH at a Zn concentration of 0.01mol/L. The amount of Zn ions removed from solution increases rapidly from pH 2 to pH 9. At pH 4, the removal efficiency of 49% of Zn ion was achieved, while at pH 9, 71% of Zn ion was removed. The reaction of

Zn ion with sulfonated poly (hydroxy styrene) polymer occurs via Ion exchange as indicated in equation 3, in addition to, the previous postulated was supported by the I.R spectral bands of polymer ligand and Zn-polymer complex as given in Figures 1 and 2 respectively. The infrared studies for the Sulfonated polymer showed additional peaks for the sulfonic acid group at 1375.75, 1 488, 631 and 600.29  $\text{cm}^{-1}$  (6). Where the conversion of infrared spectral band of sulfonic acid into sulfonic salt as clear from Figures 1 and 2, which confirm the previous postulated mechanism.

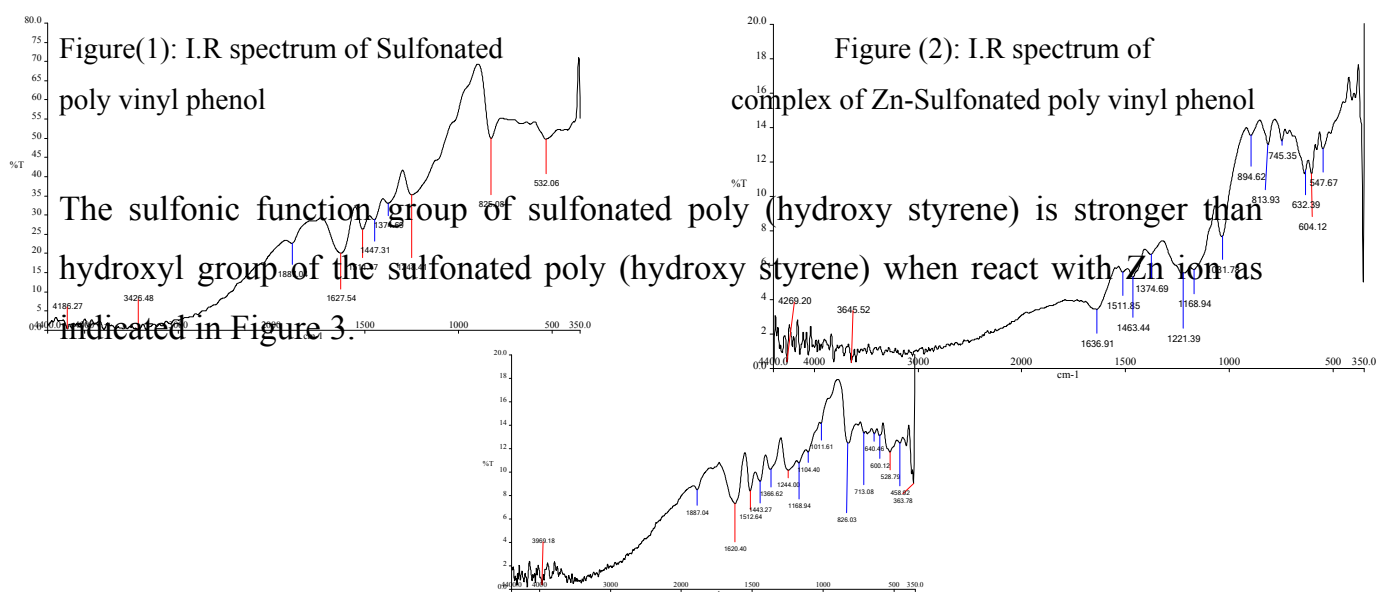
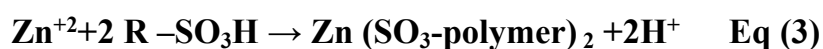


Figure (3): I.R spectrum of sulfonated poly (p-hydroxy styrene)

The maximum metal adsorbed on that polymer was 7.1 mole / g as shown in Table 1.



**NB: R -SO<sub>3</sub>H in Eq 2 represents the sulfonated poly (hydroxy styrene).**

On the other hand, Table (1) shows the amount of removal of Zinc ion using poly (p-hydroxy styrene) from aqueous solution as a function of pH at a Zn concentration of 0.01mol/L. Through look at Table 1 we can conclude that the amount of Zn ions removed from solution varied from the highest value of 41 % at pH 8 to 20% pH 4. The removal of Zn ion from solution occurs via exchange with hydroxyl function group linked to the polymer matrix of poly (p-hydroxy styrene) and represented by Eq 4.



**NB: where R-OH refers to poly (p-hydroxy styrene) polymer.**

The above reaction is enhanced by increase in the pH value due to the liberation of  $[\text{H}^+]$  as the result of exchange reaction. (7). Low sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. This means that, at higher  $\text{H}^+$  concentration, the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and metal ions. In contrast, as the pH increases, more negatively charged surface become available, thus facilitating greater metal removal. The data of removal of Ni ion using poly (4-vinyl phenol-co-methyl methacrylate) are summarized in Table 1. It is clear from Table 3 that the amounts of Ni metal ion adsorbed (Q) on poly (4-vinyl phenol -co-methyl methacrylate) polymer are ranged from 1.0 to 19.2 mole/g at pH readings of 5.0 and 9.0 respectively. This is due to at lower pH reading leads to the formation of positive charge on polymer ( $\text{R-OH}_2^+$ ) which reduce the efficiency of polymer to remove the Ni ion from the solution (8). The IR spectra of poly (4-vinyl phenol co-methyl methacrylate) and the Ni-polymer complex are given in Figures 4 and 5 respectively.

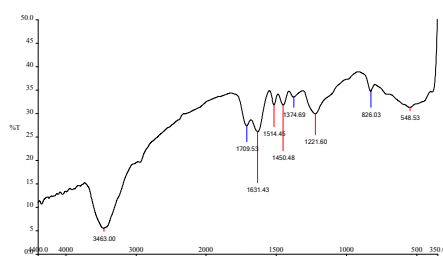


Figure (4): I.R spectrum of poly (4-vinyl phenol co-methyl methacrylate)

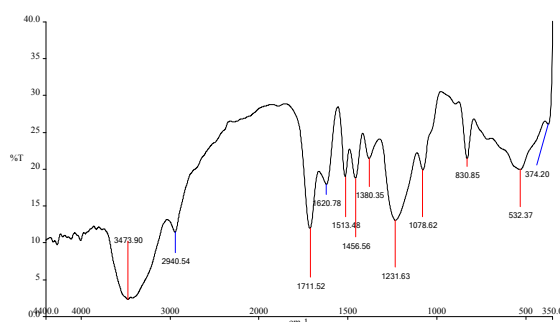
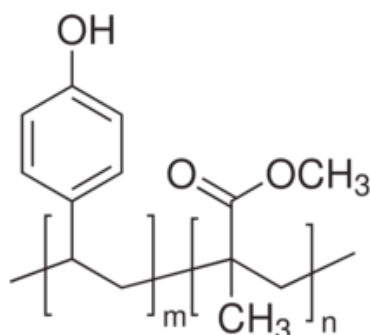
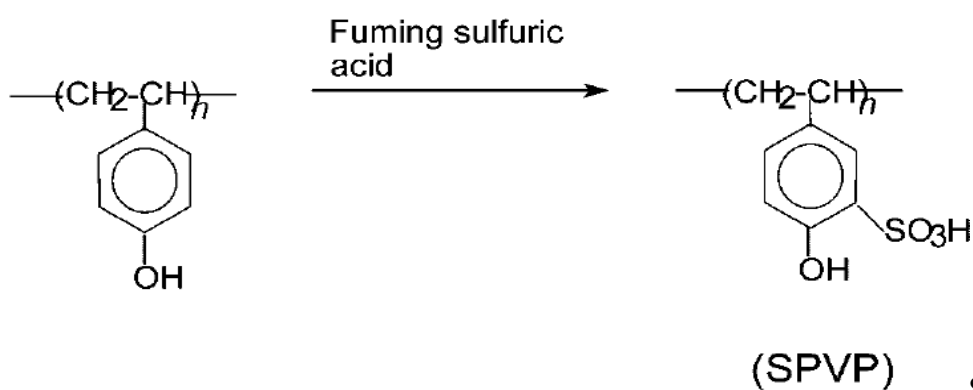


Figure (5): I.R spectrum of Ni- poly (4-vinyl phenol co-methyl

The data of Ca ion removal using poly (4-vinyl phenol co-methyl methacrylate) are shown in Table 1 which gave that the amounts of Ca metal ion adsorbed (Q) on poly (4-vinyl phenol co-methyl methacrylate) are ranged from 4.6 to 9.5 mole/g at pH readings of 9.0 and 4.0 respectively. This is mainly attributed to the precipitation of calcium ion at high pH reading (pH = 9). Therefore, the polymer could be used in removal the hardness of water at lower pH value.



Poly (4-vinyl phenol co-methyl methacrylate)



me1.Sulfonation of poly (hydroxy styrene) with fuming sulfuric acid

## Isotherm Study

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The equilibrium adsorption isotherms are important in determining the adsorption capacity of Zn (II) metal ion and diagnose the nature of adsorption onto the polymer. Two theoretical isotherm models were used to fit the experimental data: Langmuir and Freundlich models. The Langmuir and Freundlich sorption isotherms have been commonly used to describe the equilibrium behavior of adsorbate. Curves of related adsorption isotherms are regressed and parameters of the equations are provided.

### Langmuir Isotherm

The general form of the Langmuir equation is given as the following:

$$C_e/Q = 1/Q_0 b + C_e/Q_0 \quad \text{Eq(5)}$$

Where  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $Q$  is the amount of heavy metals sorbed,  $b$  is the sorption constant ( $\text{L mg}^{-1}$ ) (at a given temperature) related to the energy of sorption,  $Q_0$  is the maximum sorption capacity ( $\text{mg g}^{-1}$ ). A linear plot of  $C_e/Q$  against  $C_e$  is employed to give the values of  $Q_0$  and  $b$  from the slope and the intercept of the plot. These parameters, plus the correlation coefficient ( $R$ ), of the Langmuir equation for the sorption of Zn ion by polymer is given in Table 2.

**Freundlich Isotherm** The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as

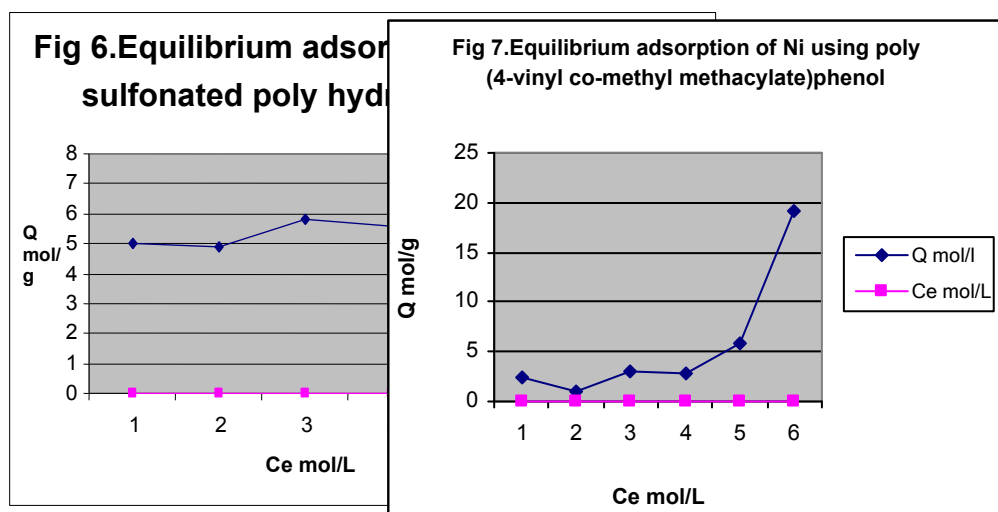
$$Q_e = K_f C_e^{1/n} \quad \text{Eq (6)}$$

The linear form of the equation can be written as:

$$\ln Q_e = \ln K_F + 1/n \ln C_e \quad \text{Eq (7)}$$



Where  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $Q_e$  is the amount of heavy metals sorbed,  $K_F$  and  $n$  are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The intercept and the slope of the linear plot of  $\ln Q_e$  versus  $\ln C_e$  at given experimental conditions provide the values of  $K_F$  and  $1/n$ , respectively. The correlation coefficient and other parameters obtained for the adsorbent are shown in Table 2, which indicates that the experimental data fitted well to Langmuir model (experimental value of  $Q=19.2$  mole/g and theoretical value was 19 mole/g for Ni while, for Zn experimental value of  $Q=7.1$  and theoretical one of  $Q=7.35$ mol/g ). This suggests that the adsorption of both Zn and Ni ions on polymer is of the monolayer-type and agrees with the observation that the metal ion adsorption from an aqueous solution usually forms a layer on the adsorbent surface <sup>(9, 10)</sup>.



Elements/polymer	W (gram)	QM/g	Efficiency %	pH	Final concentration(M)	Initial Concentration(M)
<b>Zn</b>	0.01	5	50	2	0.005	0.01
	0.01	4.9	49	4	0.0051	0.01
<b>P1</b>	0.01	5.8	58	5.5	0.0042	0.01
	0.01	5.6	56	6	0.0044	0.01
	0.01	7.1	71	9	0.0029	0.01
<b>Zn</b>	0.01	2	20	4	0.008	0.01
	0.01	2.5	25	5	0.00253	0.01
<b>P2</b>	0.01	4	40	7	0.001	0.01
	0.01	4.1	41	8	0.0009	0.01
	0.01	4.5	45	9	0.0005	0.01
<b>Ni</b>	0.01	2.5	25	4	0.0075	0.01
	0.01	1	10	5	0.009	0.01
<b>P3</b>	0.01	3	30	6	0.007	0.01
	0.01	2.8	28	7	0.0073	0.01
	0.01	5.8	58	8	0.00423	0.01
	0.01	19.2	92	9	0.0008	0.01
	0.01	5.8	58	4	0.0042	0.01
<b>Ca</b>	0.01	5.6	56	5	0.0044	0.01
	0.01	9.5	95	6	0.0005	0.01
<b>P4</b>	0.01	5.2	52	7	0.0048	0.01
	0.01	5	50	8	0.005	0.01
	0.01	4.6	46	9	0.0054	0.01
P1 is	:sulphonated poly hydroxy styrene					
P2 is	: poly hydroxy styrene					

P3 is : poly (4vinyl phenol co-methyl methacrylate)

P4 is :poly (4 vinyl phenol co -methyl methacrylate )

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**Table 1.** Removal of Zinc Nickel and Calcium ions using different polymers  
matrixes

**Table 2** The Langmuir and Freundlich isotherm models constants

Langmuir			Freundlich			
R	B	Q	* R	Kf	1/n	metal
0.99	0.275	19.35	0.96	7.2	0.23	Ni
0.98	0.175	7.35	0.97	6.2	0.12	Zn

### Conclusions

This study has demonstrated the feasibility of the modification of the poly (vinyl phenol) by reacting it with sulfuric acid to introduce sulfonic group to the phenol ring of the polymer. It was noticed that the modified polymers showed high absorption to the selected metal (Zn). Through look at Table 1 we can conclude that the amounts of Zn ion removed from solution varied from the highest value of 41 % at pH 8 to 20% pH 4. The removal of Zn ion from solution occurs via exchange with hydroxyl function group linked to the polymer matrix of poly (p-hydroxy styrene) .Low sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. This means that, at higher H<sup>+</sup> concentration, the adsorbent surface becomes more positively charged. The correlation coefficient and other parameters obtained for the adsorbent are shown in Table 2, which indicates that the experimental data fitted well to Langmuir model.

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