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Adsorption Studies of Copper (II) and Nickel (II) Ions on Polymeric Resin PMBMNen

[1]Moina Akhtar.Mughal[*], [2]Akhtar Hussain Mughal, [1]Ghulam Zuhra Memon
[3]Mohammad Yar Khuhawar and [1]Sumera Qureshi

[1]Dr. M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan
[2]Institute of Physics, University of Sindh, Jamshoro, Jamshoro, Sindh, Pakistan
[3] Institute of Advanced Research Studies in Chemical Sciences,University of Sindh, Jamshoro, Sindh, Pakistan

Abstract: - The study under investigation discovers the sorption conduct of resin used as an adsorbent toward metal ions and specified the percent sorption for the metal that reduced with rise in pH, above pH 6.The degree of uptake for resin initially was fast (88-90 %), creating equilibrium within sixty minutes for Copper. The resin exhibit the extreme percent sorption (86 - 88 %) for Nickel ranging contact time between sixty minutes; further than the described range the surge in % sorption was not recognized. The flow rate, isotherms and thermodynamic parameters were also examined for both the metal ions. PMBMNen effectively eradicated heavy amounts of metals from the real water samples.

Keywords: - *Adsorbent, column method, isotherms, Metal ion uptake, resin.*

I. INTRODUCTION

Number of reactions including heterogeneous polymerization in which motorized stirring is used for amalgamating monomer to synthesize polymers, and is used to form polymer adsorbents Formation of hyperactive cross-linked adsorbents is an example **[1,2].** As the process of adsorption proceeds in a solution the adsorbate molecule is haggard from that greater part of solution towards the adsorbent segment, remaining dominating forces like adsorbent, solute, are the reasons held responsible for the uptake **[3-5].** Catalytic flourimetric process is a widely described method regarding Cu (II) metal **[6, 7].** Researchers worldwide have tremendous contributions on chemical transformations regarding resins (polymeric) resulting enhancement in adsorption dimensions on adding different functional groups **[8-11].**

The study under investigation examines the uptake behavior of the two metals on resin PMBMNen, used as an adsorbent. Under improved conditions quantitative sorption was accomplished for the copper and nickel metal ions on prepared compound, PMBMNen. The inspected metals were desorbed magnificently with five milliliters of Hydrochloric acid (0.1M).

11. Experimental Work

The newly synthesized resin PMBMNen was recrystallized from rectified spirit to eliminate impurities and which also improved its melting point, by showing rise in melting point. The C.H.N analysis of compounds was lead at Carlo Elba Devon U.K and exposed findings that were very near to the calculated values. The uptake studies were reinforced by batch and column methods.

2.1 Batch Method

Hundred mg of hundred mesh size of polymer PMBMNen was poured in a flask that was conical comprising aqueous solutions **(**ten microgram per milliliters**)** of the metals**.** The pH of the solutions was accustomed to the desired value via adaptation of appropriate buffers. Suspension of PMBMNen on known concentration of metals (ten milliliters) were shaked with hundred rotations per minute on a thermostatic shaker.

Filtrations and several washings with deionized water were accomplished. The filtered product and washings were examined via atomic absorption spectrophotometer. The found results were used to compute the % of sorption by the compound and the (K_d) values were also evaluated.

2.2. Column Method

Five hundred milligrams of PMBMNen be located in a glass column six mm one hundred and fifty mm). The compound was adapted with twelve milliliters of Buffer possessing pH six.

II. RESULTS AND DISCUSSION

3.1 Metal ion uptake by Batch method

3.1.1) Effect of pH:

Effect of pH is a chief step in attaining the adsorption quantitatively regarding polymeric compounds. The effect of pH was speckled ranging (one to nine) for metals copper and Nickel. The more basicity of Nitrogen of C=N, group at pH directly above the said results is the cause for removing high % of metals at this raised pH, whereas at low pH protonation of azomethine group resulted. At pH six resins was capable to remove eighty eight **%** of Copper ions and eighty four **%** of Nickel metal ions. Above the said pH a fall in % sorption was perceived as shown in "Fig. 1"**.**

3.1.2 Effect of contact time/ equilibrium time

Equilibrium time was examined within the range ten to hundred minutes. Hundred mg of PMBMNen was used with hundred RPM speed of shaking, by taking twenty milliliters of ten microgram/ milliliters of both the metals. Percent adsorption of copper (II) ions was found elevated as compared to the other metal, and could be due to less action of the synthesized compound towards Nickel (II) ion .The proportion of uptake of PMBMNen in the preliminary stage was firm forming equilibrium in one hour "Fig 2".

3.1.3 Effect of Volume

The optimum volume obtained was twenty one and twenty milliliters for supreme % sorption of Cu (II) and Ni (II) ions, for PMBMNen "Fig. 3".

3.1.4 Effect of Metal ion Concentration

The sorption conduct of concentration of metal ion for the resin was calculated ranging ten to hundred µg/ml. On aggregating the concentration quantity of uptake improved and could be due to the available sites present in resin, as at greater concentrations possibility of more available sites are not obtainable for adsorption.

3.2 Metal Ion Uptake Studies by Column method.

3.2.1 Effect of Flow rate

The flow rate designated for the maximum sorption ranged within one to eight milliliters/min at the adjusted pH it was quite evident from the studies that on increasing the flow rate greater than 1 ml $min^{-1}$for the metals, the % adsorption decreased "Fig. 4".

3.2.2 Desorption

The desorption of the Cu(II) and Ni(II) metals were resulted by shaking of five hundred mg resin with the solutions of metals, on ideal conditions. The compound was filtered & washed with sum of concentrations ranged within (0.1) and (1 -10 ml) volumes of mineral acid, maximum recovery of 90 -92 % of both the metals with 0.1M Hydrochloric acid within five milliliters of volume was attained.

3.3 Adsorption Isotherms

Langmuir", "Freundlich" and Dubinin- R isotherms were applied on the data. Fruendlich plot between

log $C_{ads\,(}$mol g^{-1}) and log C_e (mol/dm^3) via using "equation 1" exhibited linearity for the synthesized resin.

$$\log C_{ads} = \log K + \frac{1}{n} \log C_e \qquad (1)$$

The curve helped in assessing the multilayer adsorption efficiency designated by K mmol g^{-1}**,** and to estimate the strength of uptake. The graph of Fruendlich isotherm exposed straight lines, as shown in "Fig.5" the intensity of adsorption 1/n was also calculated from intercept and slope on lesser balanced concentrations the adsorption capacity was repressed to approximate extent, as showed via rate of Freundlich constant 1/n is less than 1. The Freundlich constants K, n were intended as of the intercept and slope of the plot. The Langmuir constants were evaluated from intercept and slope of lined plot using "eqauion 2" as shown in "Fig.6".

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \quad (2)$$

The straight line signifies that data fitted well to the isotherm. The separation factor R_L was also considered and was found in the range that the utmost favorable separation factor for the resin PMBMNen. The Dubinin-Radushkevich isotherm was also examined for the newly formed resin was plotted among $\ln C_{ads}$ and ε^2 presented linearity using "equation 3".

$$\ln C_{ads} = \ln X_m - ß\varepsilon^2 \quad (3)$$

$$E = \frac{1}{\sqrt{-2\beta}} \quad (4)$$

The energy of adsorption, E (calculated from the slope of D-R graph) as in "Fig. 7", which is the free energy of one mole of solute to the adsorbents surface, was 12.91 for Ni (II) and 12.50 for Cu (II) ions for PMBMNen, Table [1]. The results ranged in twelve to thirteen kilo joules per mole, expected for ion exchange. The Cu (II) and Ni (II) ions were effectively sorbed on PMBMNen.

3.4 Sorption Kinetics

At the raised pH the kinetics of both the metals that is copper and nickel were assessed via alteration in sorption compared to time in (min). Morris Weber equation 5 and Lagergren equation 6 were used to calculate the results, as shown below,

$$q_t = R_{id}\sqrt{t} \quad (5)$$

$$\log (q_e - q_t) = \log q_e - \frac{kt}{2.303} \quad (6)$$

R_d the rate constant was calculable from slope of the plot, "q_t" verses "t". The graph illustrates that as the agitation time was at maximum it diverged for the metal nickel. For PMBMNen the Rd values evaluated from the slope of graph were 5.2 ± 0.05, ± 6.5 ± 0.07, 5.5 ± 0.04 and 6.7 ± 0.9 μmolg^{-1} min for both the metals "Fig. 8" & "Fig. 9".

3.5 Sorption Thermodynamics

The results of sorption were exposed to survey the parameters regarding thermodynamics, by calculating (K_c) the equilibrium constant, all the useful data regarding temperature were examined within two hundred and eighty three to three hundred and twenty three kelvin. At improved settings, for sorption of both the metal ions onto the resin, PMBMNen. The plot between log K_c was designed against 1/T (T in K) using "equation 7", providing linear relationship.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

K_c = Fe / (1 –Fe) and Fe signifies "fraction sorbed" at equilibrium. "Fig.10". The results of enthalpy and entropy were assessed via analyzing slope and intercept of the straight lined graph.

ΔH = - 18.96 ± 1.45, - 20.6 ± 2.1 kJ mol^{-1}.

ΔS = - 0.052 ± 0.002, - 0.022 ± 0.01 kJ mol^{-1} K^{-1}

ΔG at 303 K = - 4.47 ± 0.6, - 4.92 ± 0.7 kJ mol^{-1}

The negative results of ΔH, ΔS and ΔG showed spontaneity, and exothermic nature of course of sorption Table [2].

3.6 Interference Study

The influence of cations & anions sodium, potassium, Magnesium and Chloride, Bromide and SO_4 on the uptake conduct of PMBMNen *was* considered. PMBMNen was treated through fifty microgram per milliliters for the mentioned cations. The optimal pH of solution of metals was designated for the period of twenty four hours .The findings pointed out that the capacity of uptake of both the metals was not bothered by the above cations and anions.

3.7 Constancy of the Sorbent

The stability of the resin was achieved and was reprocessed ten times fluctuating among one to five percent intended for sorption, declaring the resin PMBMNen correct for "sorption".

4. Applications toward Actual H_2O Samples

For the elimination of significant metals from surface water samples, of the cultivation lands, Column technique was applied. The samples were filtered and metals were efficaciously removed under enhanced conditions from surface water samples, and were studied via Atomic Absorption spectrophotometer. The results showing percent of sorption and percent recoveries are shown in Table 3.

III. CONCLUSION

The present study focuses on newly synthesized polymeric resin PMBMNen as an adsorbent. The resin was also used to estimate the sorption capability of metal ions from surface water from different agriculture lands. The metals were desorbed well with five milliters of Hydrochloric *acid (0.1M).* The data showed that the percent of metal adsorption was greater for Copper than the Nickel complexes. The percent sorption for the metal reduced with rise in pH, above pH 6.The degree of uptake for resin initialy was fast (88-90 %), creating equilibrium within sixty minutes for Copper. The resin exhibit the extreme percent sorption (86 - 88 %) for Nickel ranging contact time between sixty minutes; further than the described range the surge in % sorption was not recognized. The *flow rate"* of one milliliter per minute was enhanced for the adsorption of metal ions on PMBMNen. The isotherms as well as the thermodynamic parameters were estimated successfully for both the metals. The data presented that the sorption capability for the metals was not pretentious by interference of diverse cations and anions. PMBMNen successfully eliminated 98% of Cu (II) and 95% of Ni (II) ions from sample 1 and 97% Cu (II) and 96% of Ni (II) ions from sample 2 and 98% of Cu (II) and 97% of Ni (II) ions from sample 3. Under heightened circumstances quantitative adsorption was accomplished for the metal ions on resins PMBMNen. The positive results gained offered an idea that such type of compounds may be prepared and can be used as adsorbents to remove substantial metals.

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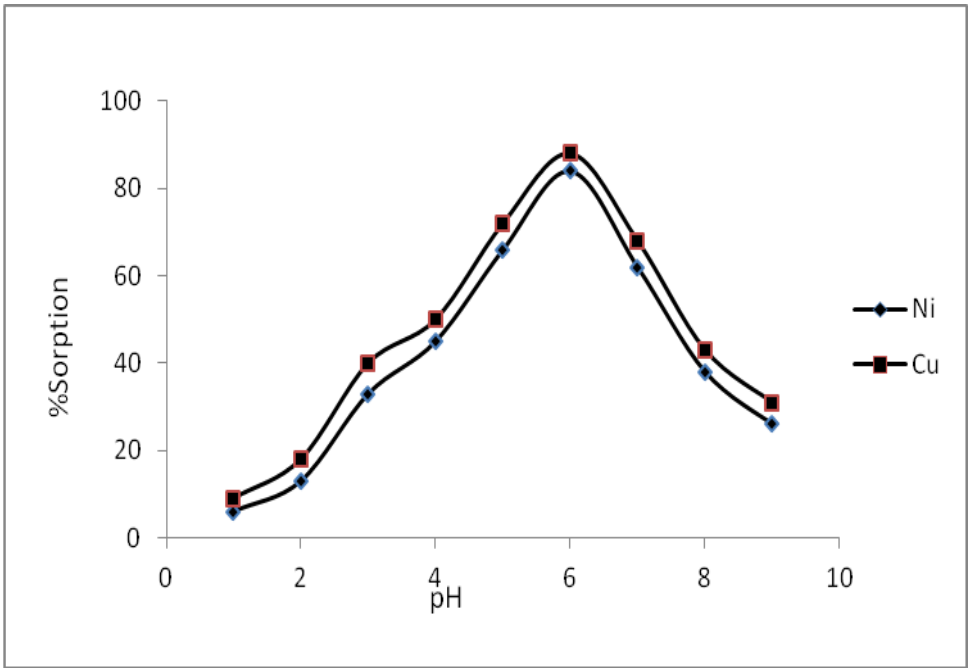

Fig: 1: Effect of pH of Resin PMBMNen for % adsorption of Cu (II) and Ni (II) in batch method.

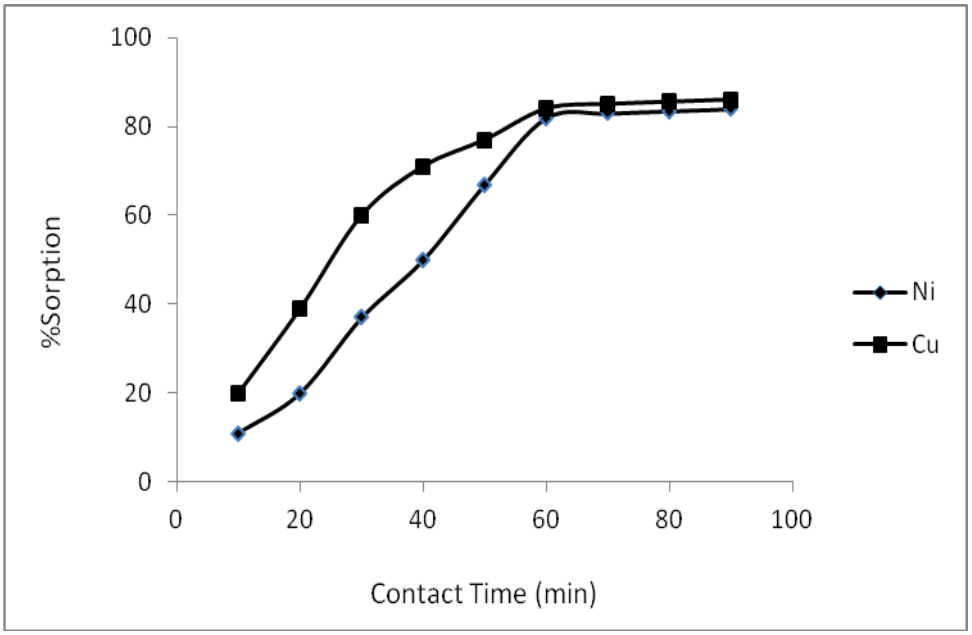

Fig: 2: Effect of Contact time on % adsorption of Cu (II) and Ni (II) ions on polymeric resin PMBMNen.

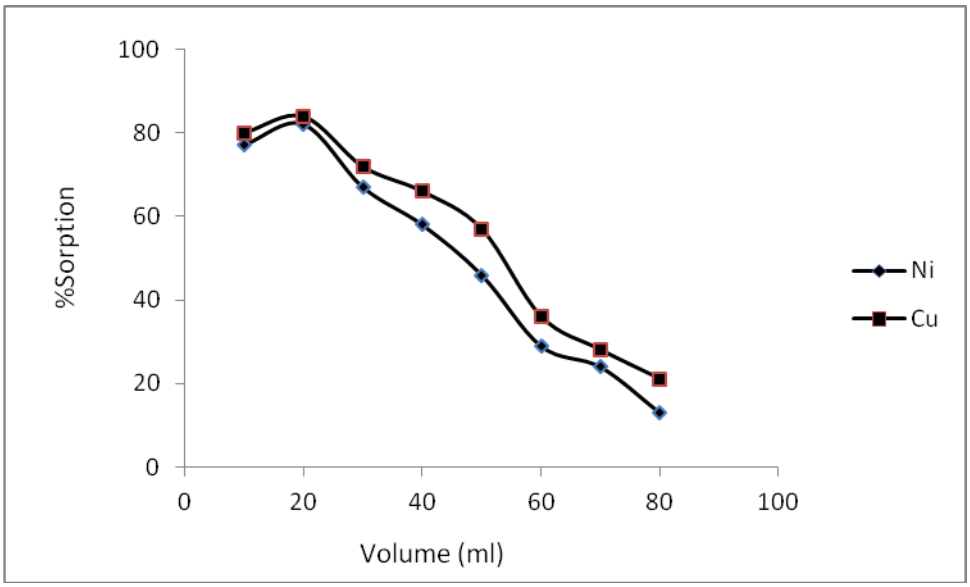

Fig: 3: Effect of volume on % adsorption of Cu (II) and Ni (II) ions on polymeric resin PMBMNen

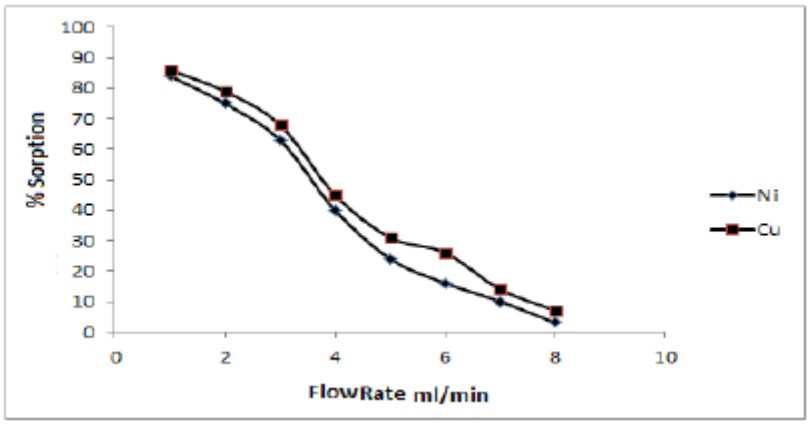

Fig: 4: Effect of flow rate on % adsorption of Cu (II) and Ni (II) ions 0n polymeric resin PMBMNen

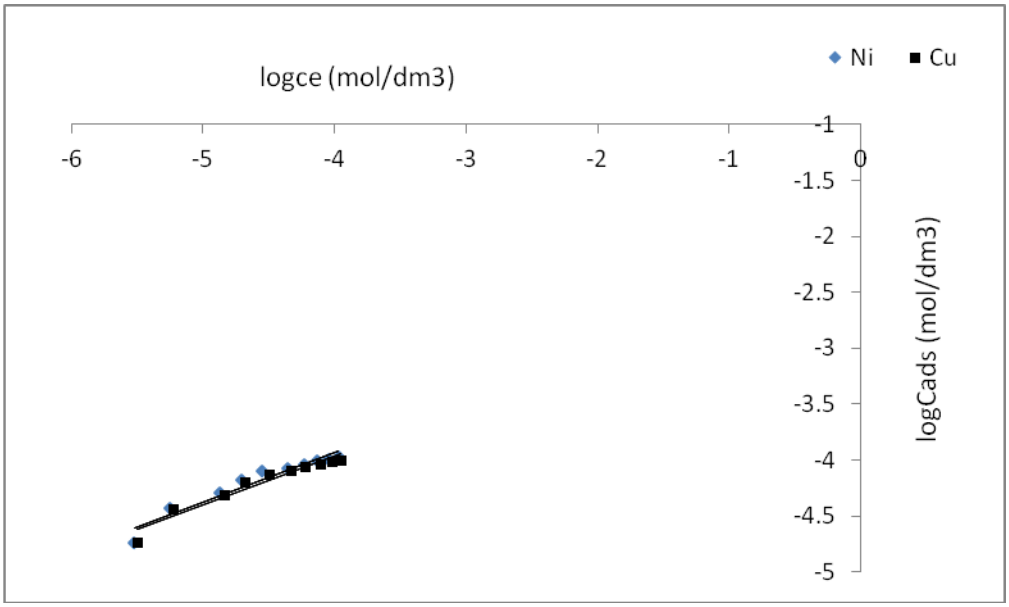

Fig: 5: Freundlich adsorption isotherm of PMBMNen for Cu (II) and Ni (II) ions.

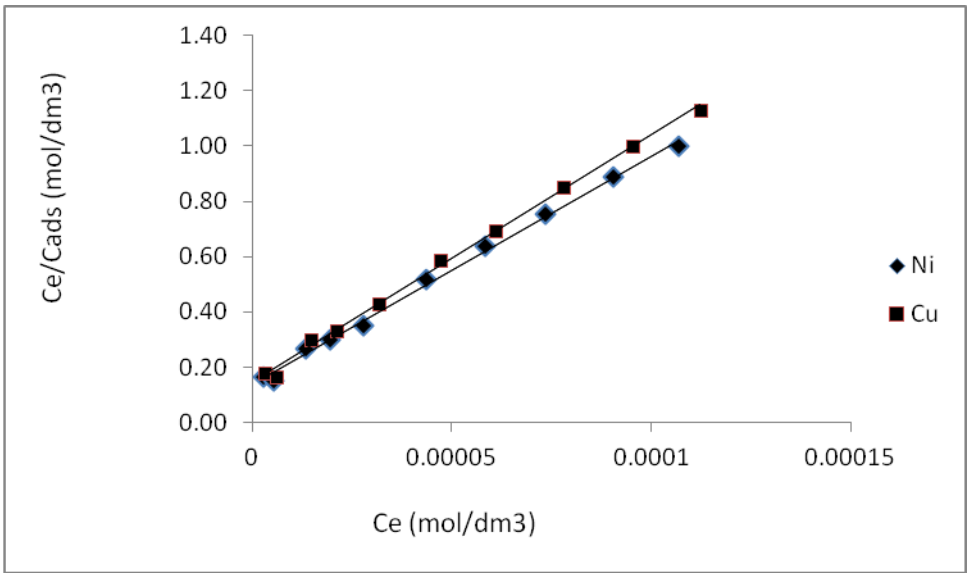

Fig: 6: Langmuir adsorption isotherm of PMBMNen for Cu (II) and Ni (II) ions.

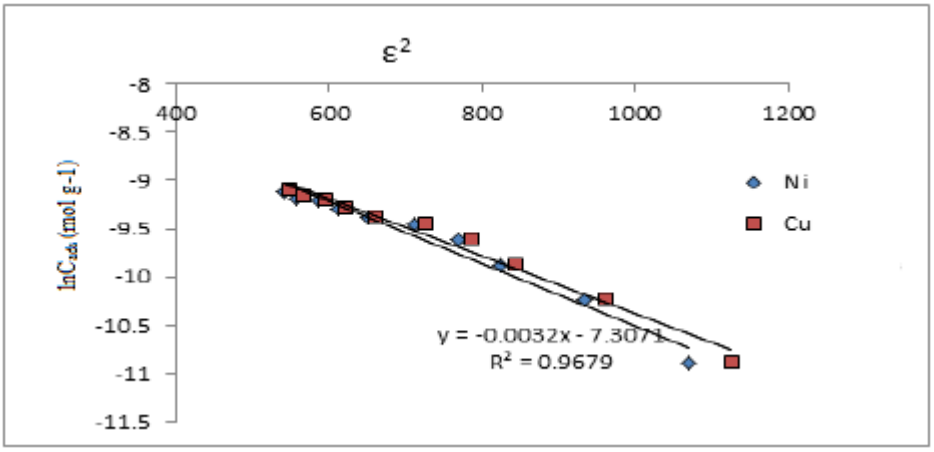

Fig: 7: D- R adsorption isotherm of PMBMNen for Cu (II) and Ni (II) ions

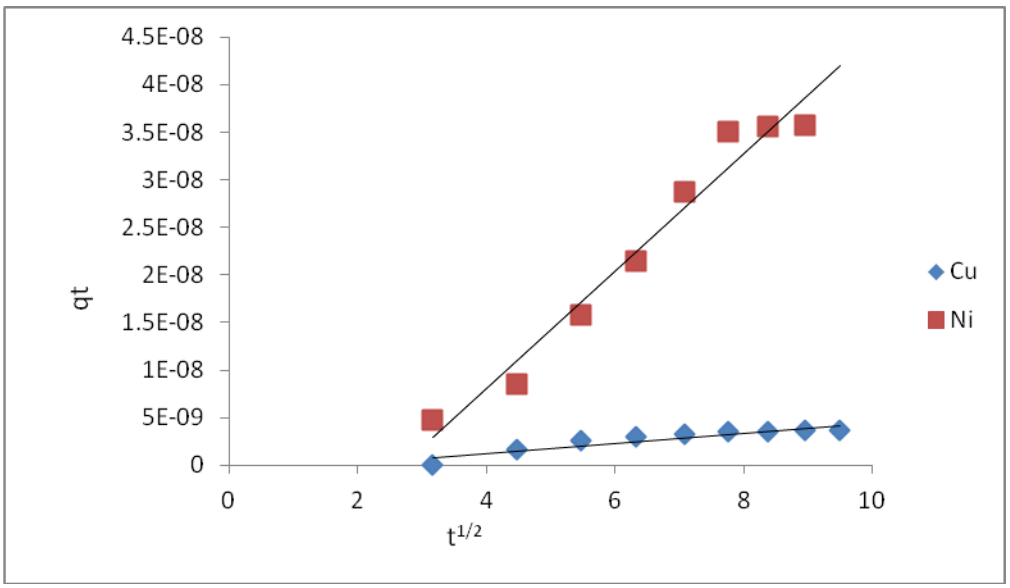

Fig: 8: Morris-Weber plot for kinetics of sorption of Cu (II) and Ni (II) ions on PMBMNen at 298 K

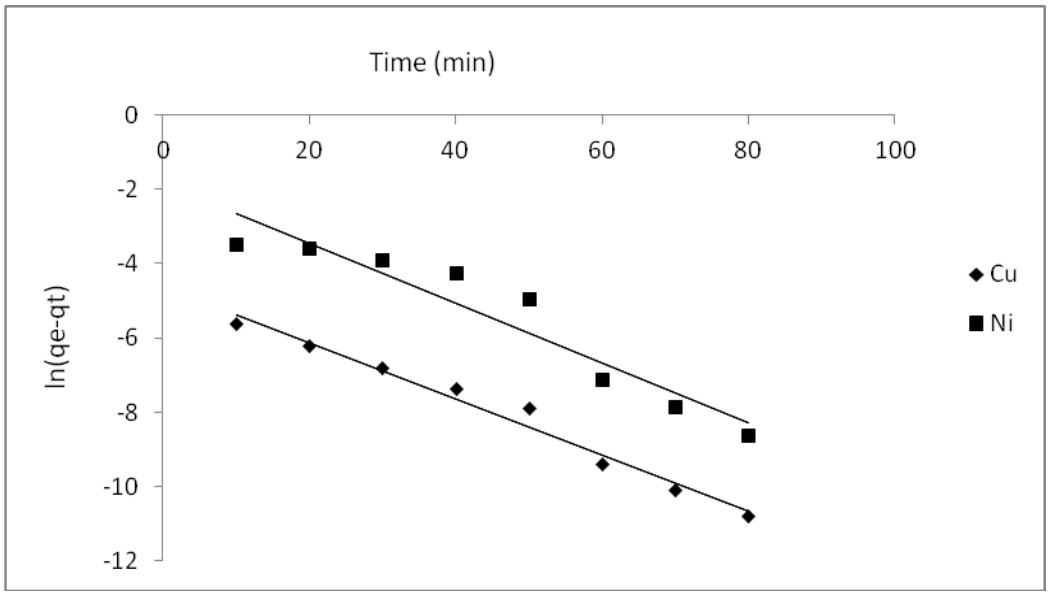

Fig: 9: Lagergren plot for kinetics of sorption of Cu (II) and Ni (II) ions on PMBMNen

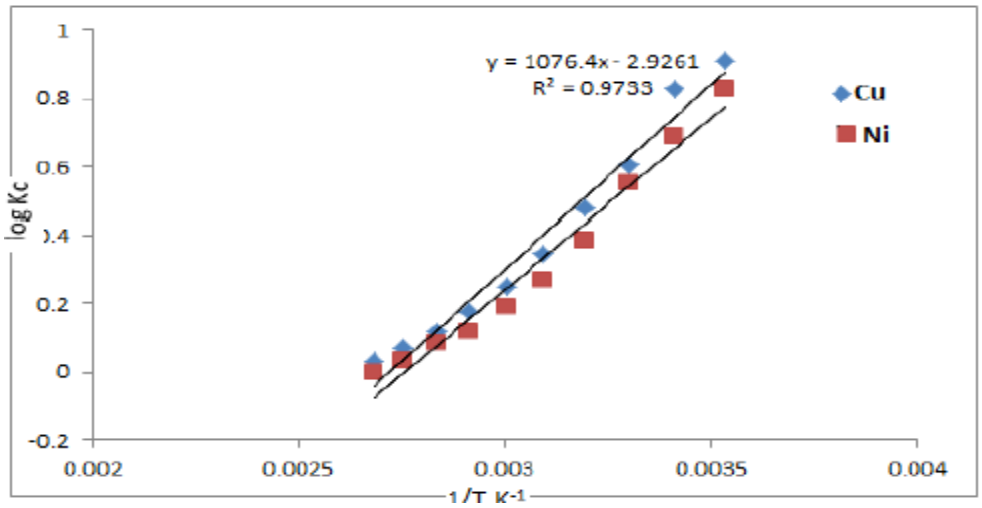

Fig: 10: Effect of temperature on sorption of PMBMNen on both metals

Table 1: Sorption Parameters of Cu (II), Ni (II) ions of Resin PMBMNen

Metal	Freundlich			Langmuir			D - R		
	K (mmol/ g)	l / n	R^2	Q (mmol/g)	B $Lmol^{-1}$	R^2	Xm mmol/g	E KJ/ mol	R^2
Cu (II)	5.9	0.43	0.934	0.112	6.1×10^4	0.997	0.59	12.50	0.952
Ni (II)	7.2	0.44	0.933	0.121	6.1×10^4	0.996	0.67	12.91	0.951

Table [2] Thermodynamic parameters for the adsorption of PMBMNen on both the metals.

Thermodynamic parameters	PMBMNen	
	Cu (II)	Ni (II)
ΔH (kJ/mol)	-20.6 ± 2.1	-18.96 ± 1.45
ΔS (kJmol^{-1} K^{-1})	-0.022 ± 0.01	-0.052 ± 0.002
ΔG_{303K} (kJmol^{-1})	-4.92 ± 0.7	-4.47 ± 0.6

Table: 3 % sorption and % recovery of Cu (II) and Ni (II) ions of real H20 samples for PMBMNen

Samples	Amount of metal ions in samples((μgL^{-1})	PMBMNen			
		Cu		Ni	
		% sorpt	% recov	% sorpt	% recov
1.	0.50 ± 0.10	98.0±0.30	96.0±0.10	95.0±0.20	94±0.10
2.	0.20 ± 0.01	97.0±0.20	94±0.30	96±0.20	94±0.10
3.	0.40 ± 0.20	98.0±0.10	96.0±0.20	97.0±0.20	95.0±0.50