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Removal of Lead, Cobalt and Manganese from Aqueous Solutions using a new Modified Synthetic Ion Exchanger

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ABSTRACT

The uptake of lead (Pb^{2+}), cobalt (Co^{2+}) and manganese (Mn^{2+}) metal ions on a synthesized ion exchange resin is performed. Para-phenol-resin is the new synthesized ion exchange resin is prepared from the polycondensation of Dioxaloyl Para sulphanilamide and phenol in the presence of 60% H_2SO_4 by weight of reactant and using glacial acetic acid as a reaction medium at 60 °C. Formaldehyde solution is added dropwise to the reaction flask in a period of 3 hours and the reaction result is finally left for 8 hours at room temperature. The resulting resin containing sulphonate ($-SO_3H^-$), and carboxylate ($-COOH^-$) acid groups Para-phenolic-resin resin is used for the removal of Pb^{2+} , Co^{2+} , and Mn^{2+} metals ions from aqueous solutions. To obtain the best heavy metal removal, batch sorption experiments are performed. Different variables are effecting the uptake of those heavy metals including, the change in the; pH, weight loading, aqueous metal ion concentrations and contact time intervals. Adsorption isotherms can be described by the Freundlich and Dubinin and Radushkevich (D-R) isotherm equations. Two kinetic models such as pseudo-first order and pseudo-second order equations are used to describe the rate of the metal ion adsorption.

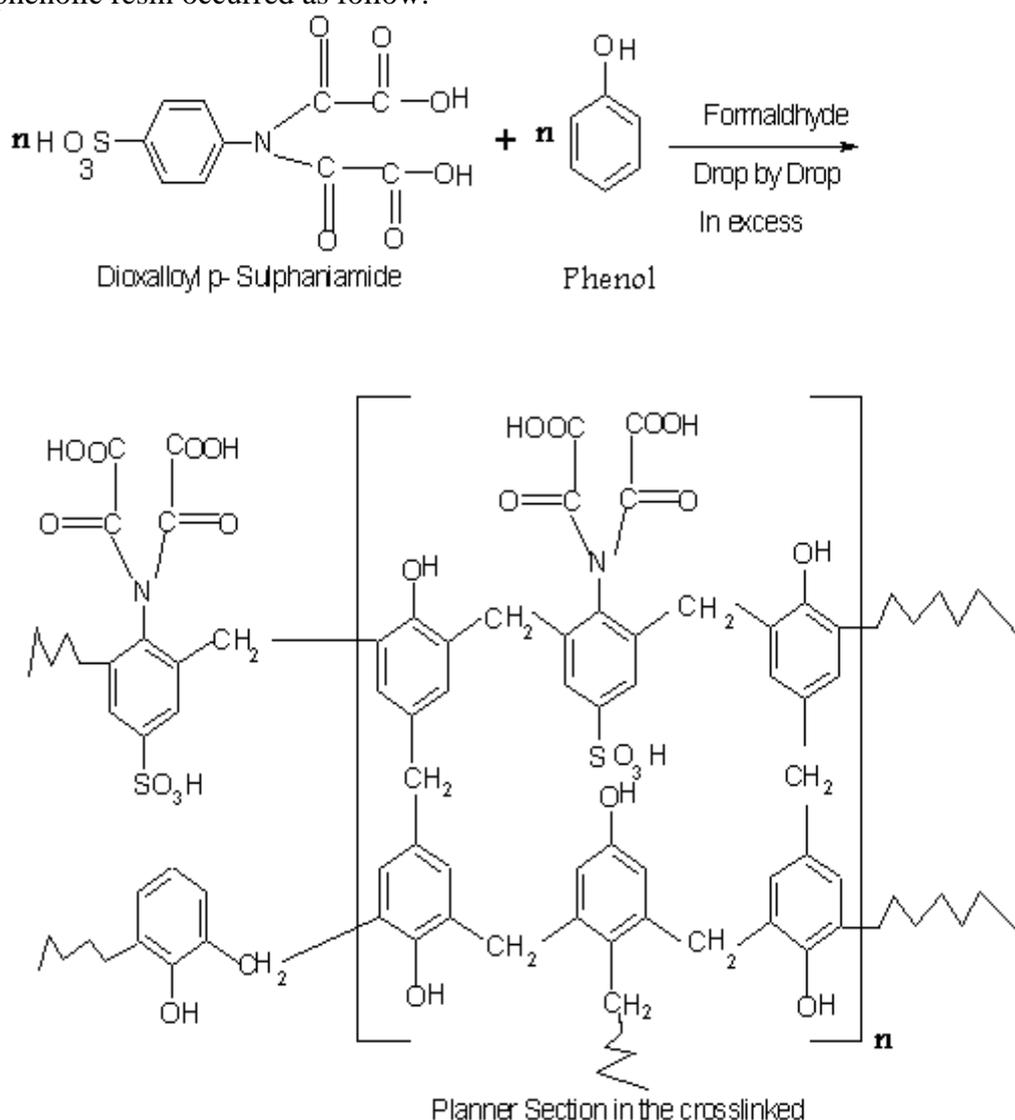
Key words: Cobalt, Lead, Manganese, ion-exchange resin.

INTRODUCTION

Various toxic heavy metal ions may discharge through different industrial activities, it constitute one of the major causes of water pollution [1, 2]. Ion exchange technique is one of the common methods that used for treatment of liquid wastes. A synthetic ion exchange resin offers an attractive and inexpensive option for the removal of heavy metal ions from aqueous solutions [2]. Modern ion exchange materials are prepared from synthetic polymers such as styrene-divinylbenzene copolymers, which have been sulphonated to form strongly acidic cation exchangers [3-5]. In ion exchange process, ions of positive charge and negative charge from an aqueous solution replace dissimilar ions of the same charge initially in the solid,

Preparation of the modified phenolic resin (Phenol- dioxaloyl p- sulphanilic acid)/ formaldehyde:

13.6 g of the produced crystalline solid was added to 300 ml of acetic acid and stirred well by a glass rod. 25 g of phenol was added to the mixture then add 30 ml of concentrated H₂SO₄ followed by the drop wise addition of 67.5 g formaldehyde in a period of 2 hours. Leave the mixture (exothermic reaction) till it attains the room temperature. The produced solid was filtered and then washed repeatedly till neutral. The solid phase was separated, dried at 110 °C, grinded and sieved to get the grain size distribution ≤ 70 μm sieve. The scheme for the modified phenolic resin occurred as follow:



Scheme (1): The synthesized cation exchange resin showing its chemical structure

Characterization of para-phenolic resin

IR, XRD and SEM

Approximately 1.0 mg of the synthesized ion exchange resin is used for pellet preparation with 60 mg KBr, the pellets is heated in an oven at 80 °C for 24 hours to reduce humidity content in the sample, this step is carried out to prevent the overlapping between water and carboxyl acid group. X-ray diffraction pattern of the prepared ion exchange resin as well as electronic microscopy are also examined.

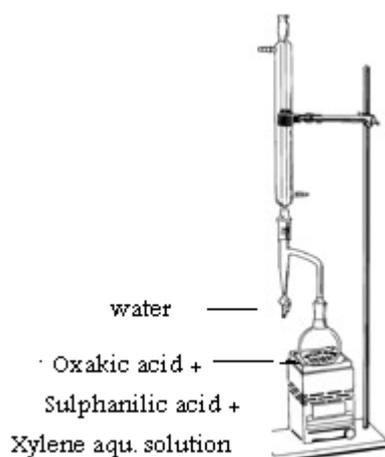


Fig. 1: The Dean and Stark apparatus

The Sorption capacity (pH titration)

A known weight of the dry solid sample (about 1.0 g) is added to 10 ml (0.01 M) of NaCl aqueous solution, this mixture is inserted in 100 ml conical flask, the flask is shaking at 30 rpm for 2 hours, titration procedure is carried out. The pH value is recorded after each addition 1.0 ml of the titrant (0.01 M of the HCl and/or NaOH aqueous solution). The mill-equivalents of H⁺ and/or OH⁻ ion concentrations gained and consumed are recorded. These values are plotted against the pH change. Adsorption capacity is calculated according to the following relationship [6]:

$$q = \frac{(C_o - C) \times V}{m} \quad (1)$$

Where, q is amount of the resin adsorbed (meq g⁻¹), C_o, and C are the initial and the final aqueous concentrations (meq ml⁻¹), V is an aqueous volume (ml), W is the dry weight of the resin (g).

Effect of pH

These experiments are carried out to determine the optimum pH that requiring for the uptake of Co²⁺, Mn²⁺ and Pb²⁺ metal ions by the synthesized phenolic resin. Batch technique is performed, 0.1 g of the synthesized ion exchange resin is added to 50 ml of double distilled water containing 25 mg L⁻¹ of aqueous Co²⁺, Mn²⁺ and Pb²⁺ metal ions. The pH of the aqueous/solid materials is adjusted prior to equilibration over the range of 2 to 10 with 0.01 M HNO₃ and 0.01 M NaOH aqueous solutions. Concentration (mg L⁻¹) of the metal ion remaining is determined using ICP-AES.

Effect of the solid loaded

Batch sorption experiments are carried out in 250 ml glass bottles, different weights (0.01 – 1.0 g) of individual synthetic ion exchange material are added to 100 ml of double distilled water containing Co²⁺, Pb²⁺ and Mn²⁺ metal ions of the concentration 25.0 mg L⁻¹. The bottles are shaken at 30 rpm for 24 h, centrifuged at 3000 rpm, then 10 ml of each aqueous solution is withdrawn, and filtered, the metal ion concentrations in the aqueous phases are determined as mmol ml⁻¹ before and after 24 hours, and the remained are calculated as mmol g⁻¹.

Effect of concentrations

Batch sorption experiments are carried out in 250 ml glass bottles, 0.1 g of individual synthesized ion exchange material is added to 100 ml of aqueous solutions containing Co^{2+} , Pb^{2+} and Mn^{2+} ions concentrations (0.5 – 25 mg L^{-1}). these mixtures are inserted in several bottles, the bottles are shaken at 30 rpm for 24 h, centrifuged at 3000 rpm. Concentrations of the ions dissolved in solutions (mmol L^{-1}) and that adsorbed (mmol g^{-1}) are calculated.

Kinetic experiments

Batch sorption experiments are conducted. About 1.0 g of individual solid sample is mixed with 100 ml aqueous solution of the $^{+}$ metal ion concentrations 25.0 mg l^{-1} of Co^{2+} , Pb^{2+} and Mn^{2+} , these mixtures are inserted in 200 ml glass bottles, the bottles are shaken at 30 rpm for different contact time intervals ranged , 1, 2, 3 h,.....to 24 h at 30 °C, these bottles are centrifuged at 3000 rpm, then the solutions are withdrawn, concentrations of the ions dissolved in aqueous phases are calculated as meq ml^{-1} , and those ions remained are calculated as meq g^{-1} .

Theoretical Concepts:*Langmuir isotherm*

The linear form of the Langmuir equation [7] is given as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{K_L Q_o C_e} \quad (2)$$

Where q_e is amount of the solute adsorbent (mmol g^{-1}), C_e is an equilibrium of ion concentration in the solution (mmol l^{-1}), Q_o is the maximum surface capacity of a monolayer coverage and K_L is the Langmuir adsorption constant ($1/\text{mmol}$). When the plot $\frac{1}{q_e}$ against

$\frac{1}{C_e}$ is given by the straight line with a high correlation coefficient, the result indicate that the adsorbed solute obeys the Langmuir isotherm of monolayer adsorption. The values of Q_o and K_L can be calculated from the intercept and the slope of the straight line relationship

Freundlich isotherm

This model is given by the multilayer of heterogeneous adsorption [8] as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

K_F is the Freundlich constant (mmol g^{-1}), n is an integer factor.

The linear form of the Freundlich equation can be obtained by taking the logarithms of Eq. 3 as follows:

$$\text{Log } q_e = \text{log } K_F + \frac{1}{n} \text{log } C_e \quad (4)$$

The plot of $\text{log } q_e$ against $\text{log } C_e$ will be given by a straight line relationship with a high correlation coefficient, K_F and n values can be calculated from the intercept and the slop of the straight line relationship.

Dubinin and Radushkevich (D-R) isotherm

The Dubinin and Radushkevich [9] isotherm equation is expressed as:

$$q_e = b \exp (-K \varepsilon^2) \quad (5)$$

or the linear form of this equation is given as:

$$\ln q_e = \ln b - K \varepsilon^2 \quad (6)$$

Where q_e is the equilibrium ionic concentration on the solid phase (mol kg^{-1}), b is the maximum sorption capacity, K is a constant related to the sorption energy ($\text{mol}^2 \text{J}^{-2}$), and ε is the polonyi potential (J mol^{-1}).

$$\varepsilon = R T \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

Where, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \cdot \text{K}$), T is the absolute temperature and C is the equilibrium concentration of ion in the bulk solution (mol m^{-3}), where $\text{m}^3 = 1000 \text{ liter}$. Plots of $\ln q_e$ against ε^2 should give a straight line for the D-R isotherm.

The slope of the straight line is given by K , where K is related to the mean energy of the uptake. The mean energy is calculated as:

$$E = (-2K)^{-0.5} \quad (8)$$

Kinetic studies*Pseudo- first order model*

Pseudo- first order model is represented by Lagergren rate equation [10, 11] as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (9)$$

or its linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (10)$$

Where, k_1 is the pseudo first order rate constant and t is the time (min.). q_t is the amount of metal ions sorbed at any given time (mg g^{-1}) and q_e is the amount of metal ions sorbed per unit weight of the species (mg g^{-1}) at equilibrium (sorption capacity).

qt and qe can be estimated by the following relations:

$$qt = (C_o - C_t) \frac{V}{m} \quad (11) \quad \text{and} \quad qe = (C_o - C_e) \frac{V}{m} \quad (12)$$

Where, C_o is the initial liquid phase concentration of the solutes (mg/g), C_t is the solute concentration at time t (mg g^{-1}), V is the aqueous volume (liter) and m is mass of the soil sample (g).

Plots of $\log (q_e - q_t)$ versus t should give a straight line and the constant (k_1) could be calculated from the slope of the straight line.

Pseudo-second order

Pseudo-second order model [11] is expressed as:

$$\frac{dq_e}{dt} = k_2 (q_e - q_t)^2 \quad (13)$$

Or by its linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

k_2 is the pseudo second order rate constant (mg /min).

the plotting of t/q_t against t would give by a straight line, the intercept and the slope of the line correspond to the rate constant (k_2) and the sorption capacity (q_e) respectively.

RESULTS AND DISCUSSION

The exchange capacity of the synthesized ion exchange resin (para-phenolic resin) in its hydrogen form and other physical properties are given in Table 1. It is observed that para – phenolic resin has a high specific surface area value, $5.2 \text{ m}^2 \text{ g}^{-1}$, the exchange capacity values 3.0 and 1.1 meq g^{-1} , these values are corresponding to the strong SO_3H^- and the weak – COOH^- ionogenic functional groups.

Table 1: The physical parameters of the Para-phenolic-ion exchange resin.

Parameter	Value
Specific cation exchange capacity	3.0 and 1.1 meq/g
Particle size	170 μm
Density	1.4 ± 0.01
Specific surface area	$5.2 \pm 0.01 \text{ m}^2/\text{g}$
The ionogenic Functional groups	$-\text{COOH}^-$ & HSO_3H^+

The Infra red absorption bands are given in Figure 2, and show the following absorption bands. The strong absorption band appeared at 686 cm^{-1} , the results are attributed to the bending deformation of SO_2 group. The absorption band appearing at 835 cm^{-1} may be attributed to the multisubstituted of benzene ring (C-H group) out of the plane deformation. The strong absorption band appearing at 1423 cm^{-1} is due to the symmetric stretching vibrations for CH_2 group, other strong absorption band appearing at 1601 cm^{-1} can be attributed to the symmetric stretching vibration for $\text{C} = \text{C}$ in benzene ring. The strong absorption band appearing at 1631 cm^{-1} is due to stretching vibration of the carbonyl group in region of ($\text{N}-\text{C} = \text{O}$) group. The medium absorption band at 1732 cm^{-1} is due to stretching vibration of the carbonyl group in free carboxylic group. The broad band appearing at 3300 to 2648 cm^{-1} is due to the overlap of OH group at the sulphonic and carboxylic acid groups. X-ray diffraction pattern indicate that the modified ion exchange resin has amorphous structure, (i.e. there is no peaks in the region of organic compounds at 2θ - 20 - 30°).

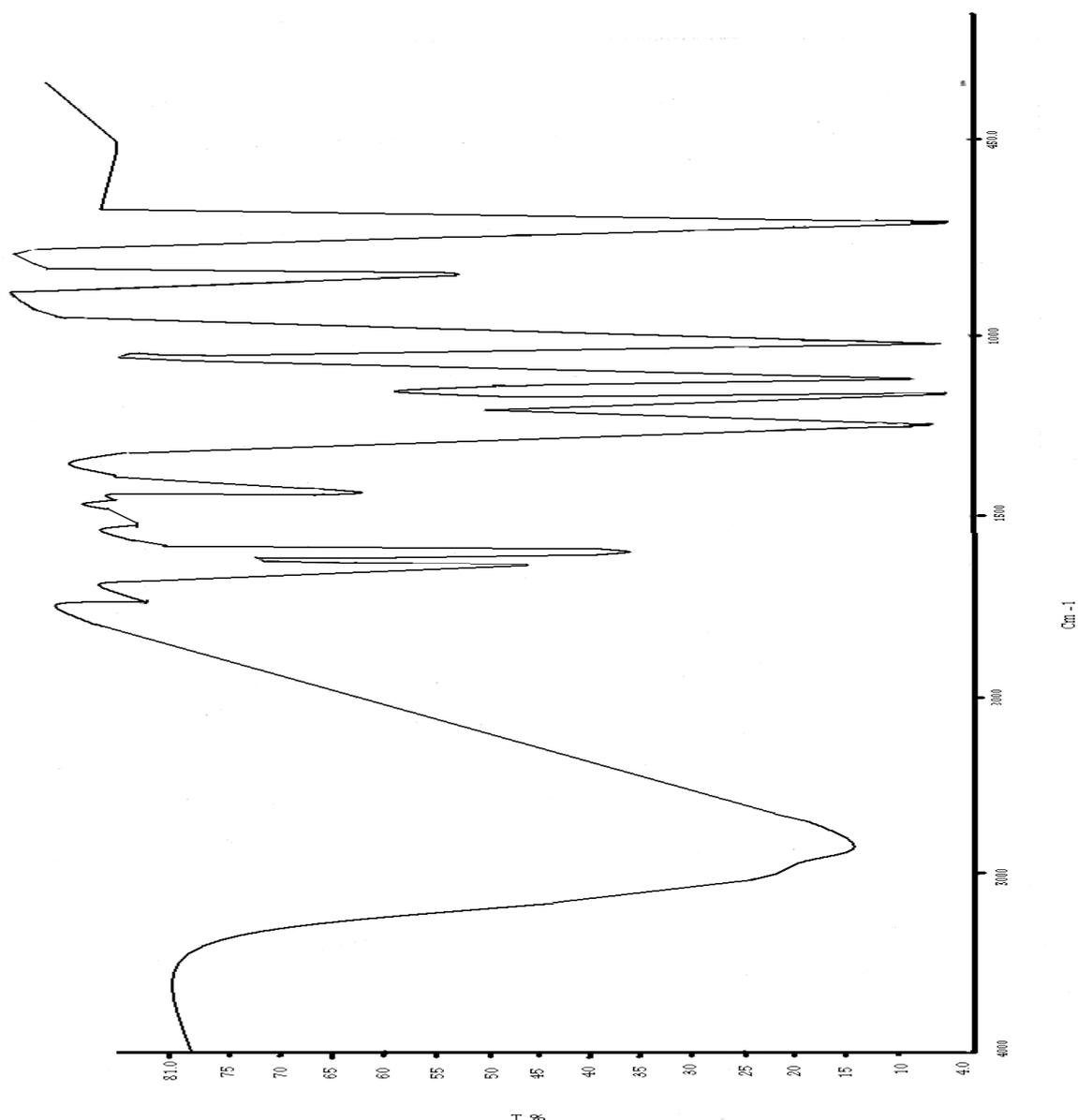


Fig. 2: Infra-red of the synthetic para –phenol resin

The Scanning electron microscope of the bulk synthesized ion exchange resin is given in Fig. 3, while Fig. 4 gives the sector of this ion exchange resin, the scanning electron microscopy are generally used to detect the topography of the resin grain surface and the molecules orientation in the space. From these Figures, it is clear that the prepared ion exchange resin has a micro tubular structure.

Sorption studies

Effect of pH

Variation of the metal ions (Co^{2+} , Pb^{2+} and Mn^{2+}) uptake with pH has shown in Fig. 5. The adsorption capacities (mmol g^{-1}) are found to be low at the lower pH values and increased with increasing of the pH. these results indicate of that metals are poorly adsorbed at the low pH values, this contribution may be accounted by the competitive adsorption of H_3O^+ ions and the metal ions for the same active sorption sites. As the pH increased, the uptake on the solid surface is increased. The pH values 5-7 are the optimum pH for the metal ions Co^{2+} , Pb^{2+} and Mn^{2+} sorption capacity, electrostatic attraction between the metal ions in solution

with the solid is increased at these pH values. The increasing of adsorption by the increase of the pH is due to the release of OH⁻ ions these results are in a good agreement with the obtained data by Pehlivan et al [12].

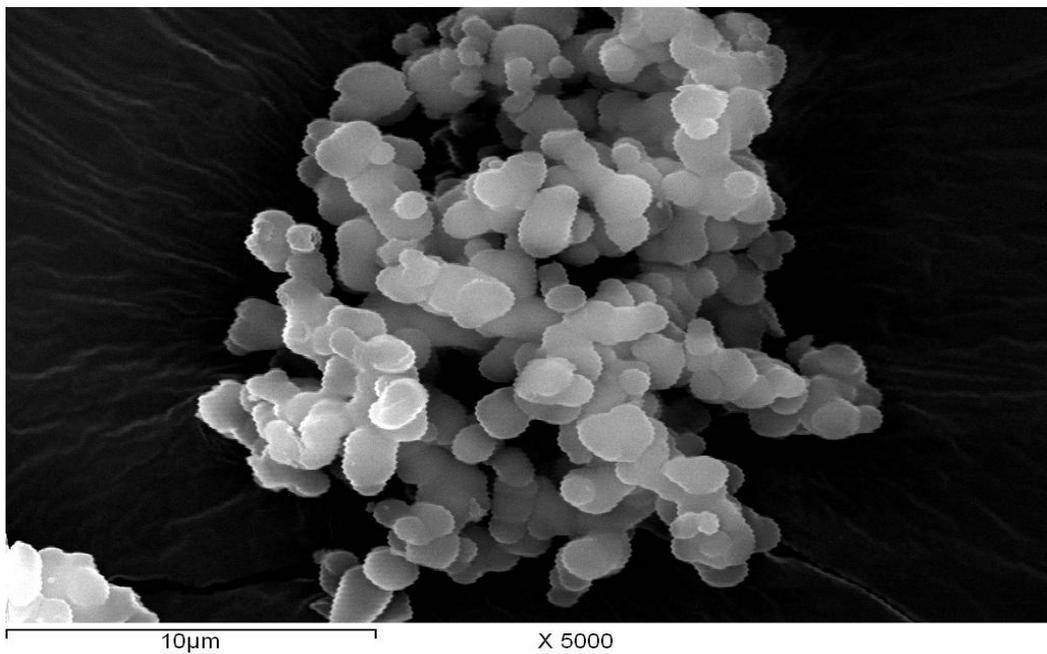


Fig. 3: The Scanning Electron Microscope of the Bulk synthesized Ion Exchange Resin.

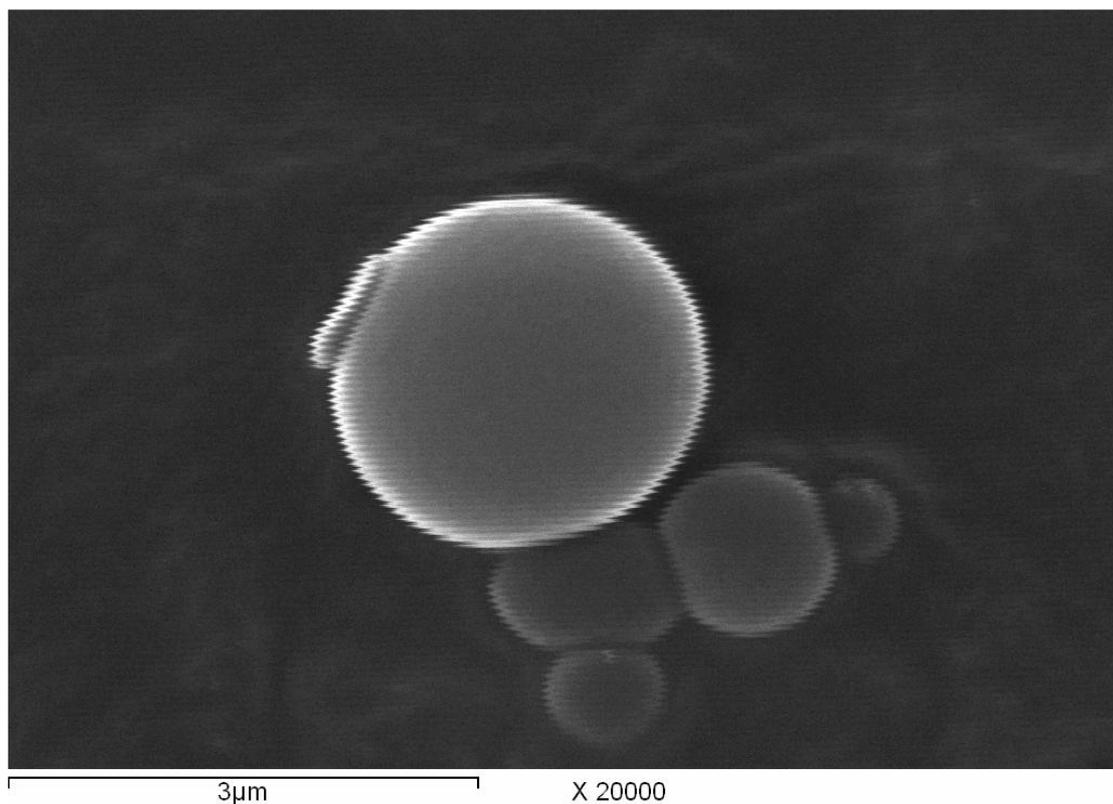


Fig. 4: The Scanning Electron Microscope Sector of the synthesized Ion Exchange Resin.

Effect of weight loaded

The uptake of the metal ions Co^{2+} , Pb^{2+} and Mn^{2+} (mmol g^{-1}) is plotted as a function of resin weight. Figure. 6 show that the sorption capacities increases as the amount of ion exchange loaded is increased. The optimum weight for the metal sorption capacities was found to be 0.1 g of resin weight. These results are expected because the fixed initial metal concentration increases by increasing of the adsorbed sites [12].

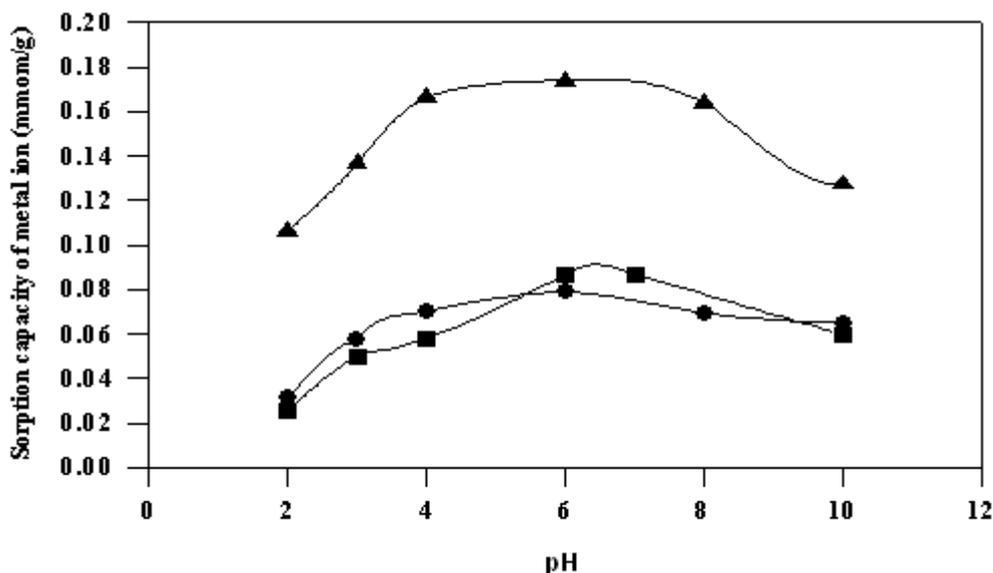


Fig. 5: Effect of pH change on the sorption capacities

● Co, ■ Pb and ▲ Mn ions

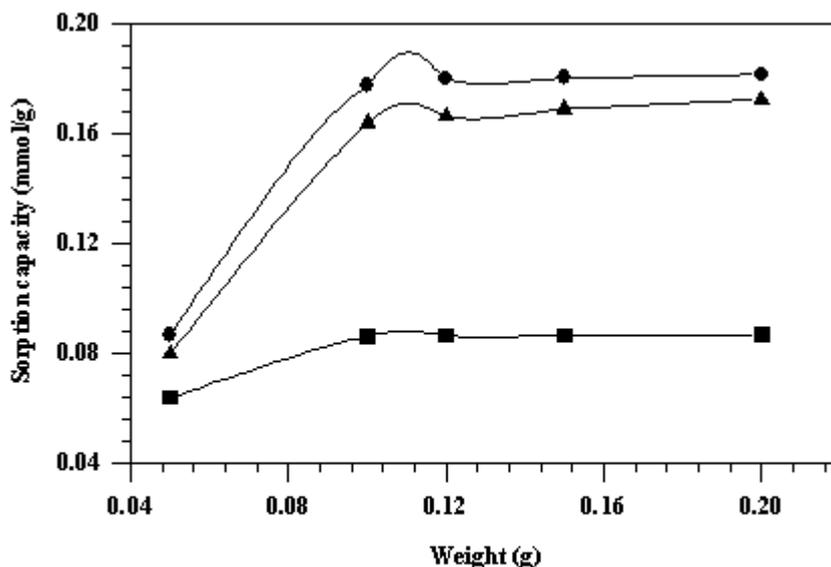


Fig. 6: Effect of weight on the sorption capacities

● Co, ■ Pb and ▲ Mn ions

Effect of concentrations

The effect of initial concentrations on the metal ions uptake is investigated by varying initial concentrations of the metal ions at an optimum pH value 7 and 1 h of equilibrium time, the sorption data are not given by the straight line of the Langmuir equation, therefore the data are not well agree with the Langmuir adsorption isotherm.

The Freundlich isotherm is obtained from the plots of $\log q_e$ vs. $\log C_e$ for adsorption of Co^{2+} , Pb^{2+} and Mn^{2+} metal ions, onto para-phenolic resin. Figures (7-9) employed to determine the intercept values of $\log KF$ and the slope of $1/n$. Table 2 gives the Freundlich constant (KF) values, these values are changed from 0.087, 0.848 and 0.475 for cobalt, lead and manganese sorption. Moreover, the values of n is given from the slope of the straight line relationship. It has the values 0.75, 0.84 and 0.906 the slopes of the straight line is less than one value, it is indicated that the Co^{2+} , Pb^{2+} and Mn^{2+} metal ions have good adsorption onto the synthesized para-phenolic resin, similar studies are performed on application of the Freundlich isotherm for removal of Pb ions species from aqueous solution by other ion exchange resin [13]. The slope of the Freundlich isotherm, n , is also denoting to the strength of adsorption process and the distribution of active sites. If $N < 1$, bond energies increase with the surface density, if $N > 1$, bond energies decrease with the surface density, and when $N = 1$, all surface sites are equivalent [14]. Figures (10-12) give the plots of $\ln q_e$ (mol g^{-1}) against ϵ , for an equilibrium sorption of Co^{2+} , Pb^{2+} and Mn^{2+} ions with the solid phase, these Figures are well described by the D-R straight line equation. Table 2 gives the isotherm parameters of the Freundlich and D-R isotherm equations. The mean energy (E) is calculated. The magnitude of E is useful for estimating the type of sorption reaction. These energies are found to be 11.2 – 13.0 which are within the energy range of ion exchange reaction 8-16 kJ/mol [15, 16].

Table2: Freundlich and D-R sorption isotherms Parameters

Species	Cobalt				
	K	N	B (mol/g)	K (mol^2/kJ^2)	R ²
Freundlich sorption isotherm	1.219	0.750	-	-	0.991
D-R sorption isotherm	-	-	6.3×10^{-7}	0.004	0.993
Species	Lead				
Freundlich sorption isotherm	7.063	0.841	-	-	0.983
D-R sorption isotherm	-	-	1.6×10^{-6}	0.003	0.993
Species	Manganese				
Freundlich sorption isotherm	2.999	0.906	-	-	0.995
D-R sorption isotherm	-	-	6.6×10^{-7}	0.0035	0.991

Kinetic studies

The uptake of Pb^{2+} , Co^{2+} and Mn^{2+} metal ions (meq/g) on the new modified ion exchange resin is determined after different contact time intervals. Figure 13 shows the experimental sorption capacity (meq g^{-1}) values (q_{exp}) vs. different contact time intervals. Fast reaction is observed after the short time intervals from 1 to 6 minutes, then the rate of the uptake is increased slowly with the increasing of time. After ~ one hour, an equilibrium state is attained. The sorption capacities (meq g^{-1}) are decreased by the following order: $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$. The pseudo-first order and the pseudo-second order kinetic models are applied to the experimental data. Plotting of $\log (q_e - qt)$ against different contact time intervals (t). The results are given by the straight lines relationships (Fig 14). The slopes and the intercept, k_1 and q_e along with the correlation coefficient (r^2) values are given in Table 3. A comparison of the sorption capacity value for the experimental and the pseudo-first order kinetic equation are given in Table 3, the values indicated that the metal ions adsorption data does not follow by the pseudo-first order kinetic mode quite satisfactory and the values are posses also fairly low when compared with the experimental values (Fig. 13). Plotting of t/qt against t for Pb^{2+} , Co^{2+} and Mn^{2+} ions species are given by the straight lines relationships with the high correlation coefficients near to one value, Figs (15-17). The intercept and the slope of the straight line relationships are given by the rate constant (k_2) and the sorption capacity (q_e)

respectively, the theoretical q_e of the pseudo-second order kinetic values agree perfectly well with the experimental q_e data.(Fig. 13) at equilibrium.

Many applications of the ion exchange are carried out for removal of some heavy metals from aqueous solutions. The removal of Co, Mn and Pb from tap water is carried out with a cation exchange resin possessing a chelating iminodiacetic acid group [17].

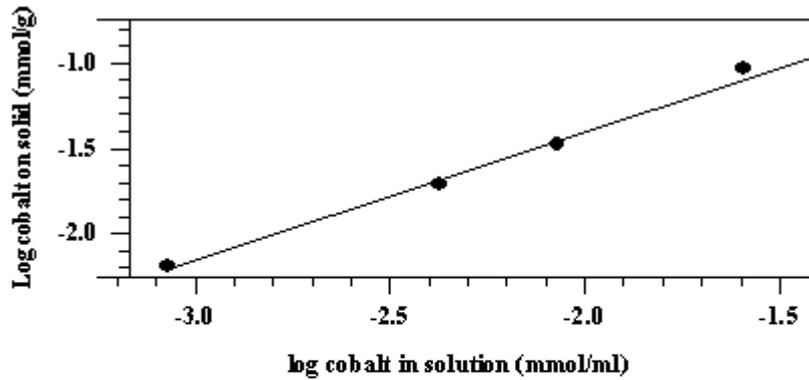


Fig. 7: Freundlich isotherm of cobalt sorption on the exchange resin

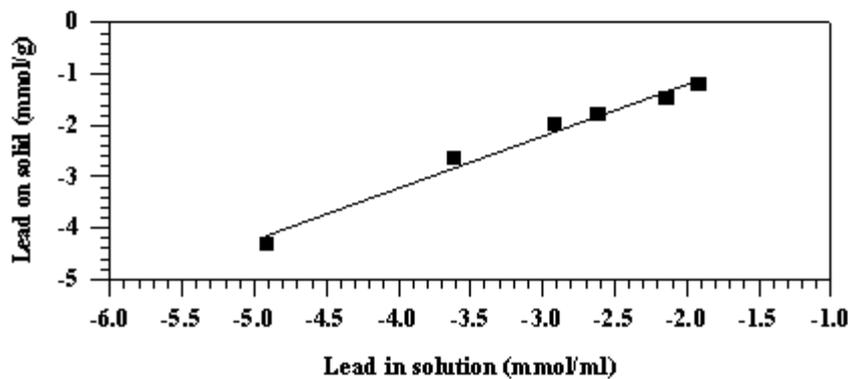


Fig. 8: Freundlich isotherm of lead sorption on the exchange resin

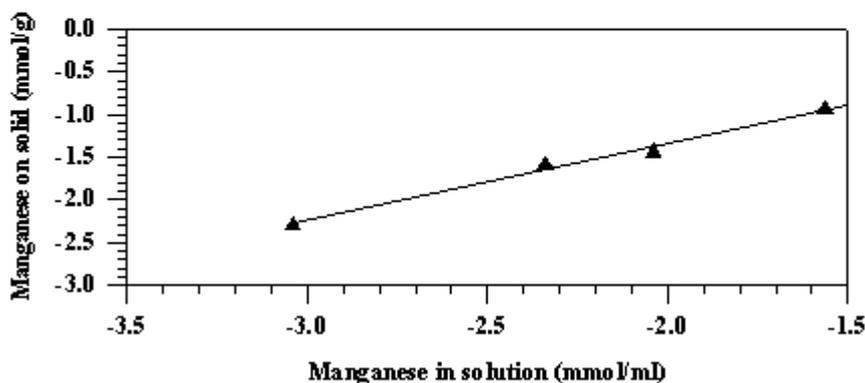


Fig. 9: Freundlich Isotherm of manganese sorption on the exchange resin

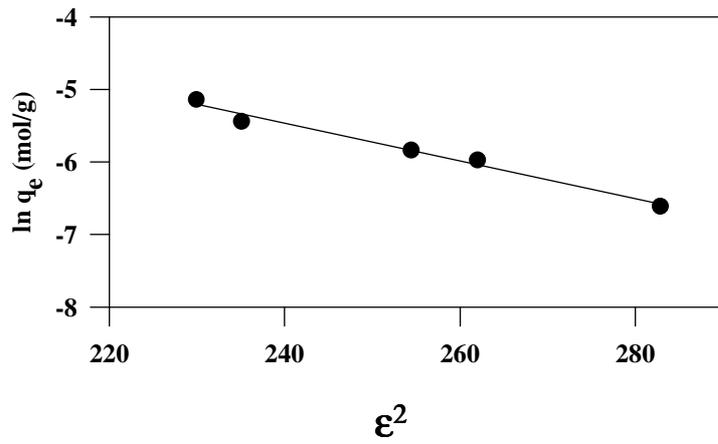


Fig. 10: D-R isotherm of sorption cobalt ions

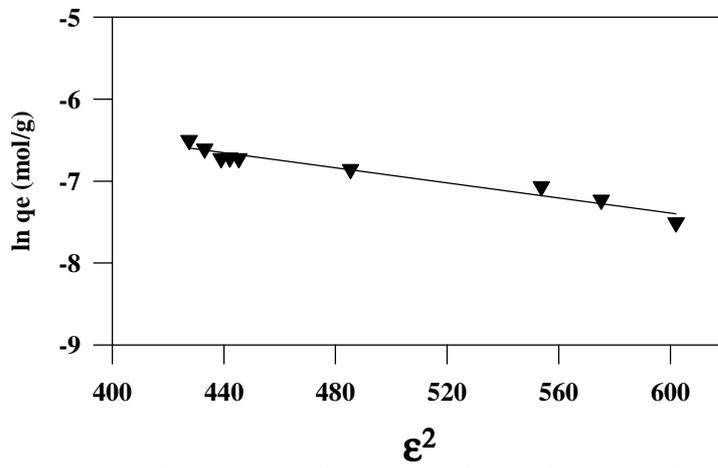


Fig. 11: D-R isotherm of sorption lead ions

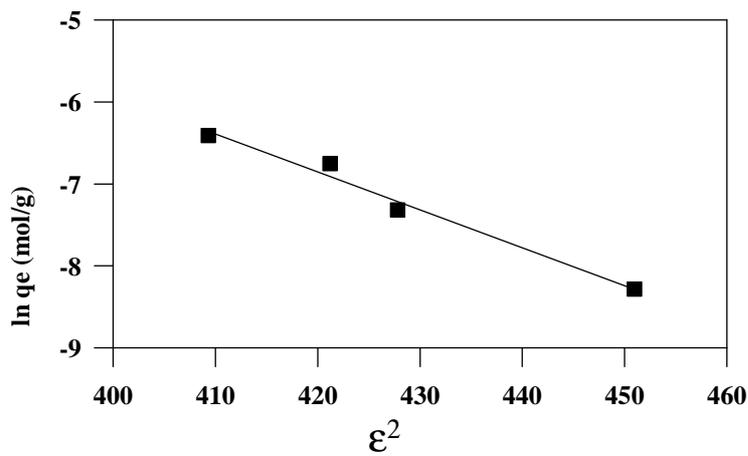
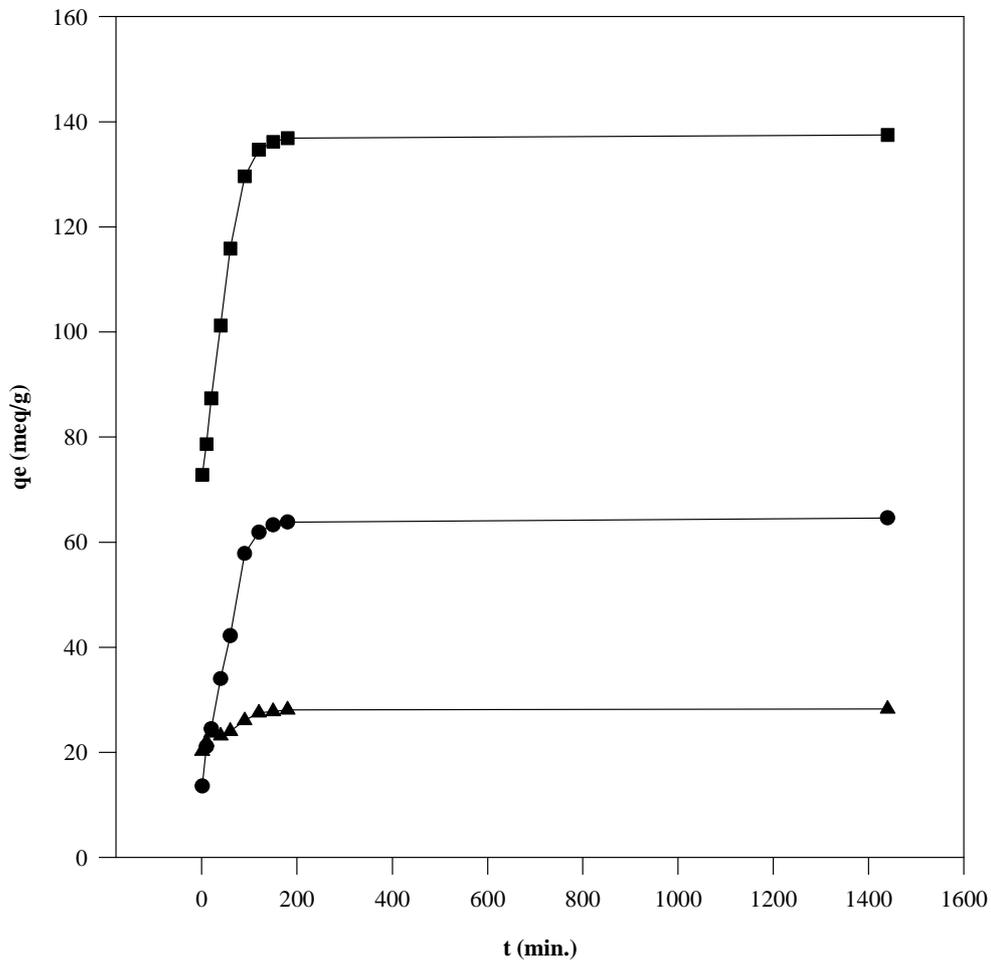


Fig. 12: D-R isotherm of sorption manganese ions



**Fig. 13: The sorption capacities of the ; —●— Co(II) species,
 —■— Mn(II) and —▲— Pb species as a function
 different contact time intervals**

Application of the pseudo-first order and the pseudo-second order kinetic equations are performed for the adsorption of heavy metal ions onto biopolymeric material [6]. Cobalt adsorption on lemon peel adsorbent can be described more favorably by the pseudo-second order kinetic model[18], and the kinetics of other pollutant sorption by biosorbents are reviewed using other studies[19].

Table 3. Comparison between the sorption capacity values (qe) which calculated from application of pseudo-first-order and pseudo- second-order models with the the experimental values for the metal ions Pb²⁺, Co²⁺ and Mn²⁺ (meq/g) adsorption.

Element	Initial conc. (mol/l)	Pseudo-first-order model			
		$q_e (exp.)$ (mmol/g)	$q_e (calc.)$	r^2	K_1
Lead (Pb ²⁺)	121×10^{-4}	0.180	0.138	0.961	0.0207
Cobalt (Co ²⁺)	417×10^{-4}	0.086	0.074	0.966	0.0184
Manganese(Mn ²⁺)	455×10^{-4}	0.058	0.026	0.963	0.0124
Element	Intial conc. (M)	Pseudo-second-order model			
		$q_e (exp.)$	$q_e (calc.)$	r^2	K_2
Lead (Pb ²⁺)	121×10^{-4}	0.180	0.179	0.990	0.581
Cobalt (Co ²⁺)	417×10^{-4}	0.096	0.113	0.990	0.147
Manganese(Mn ²⁺)	455×10^{-4}	0.058	0.057	0.992	2.192

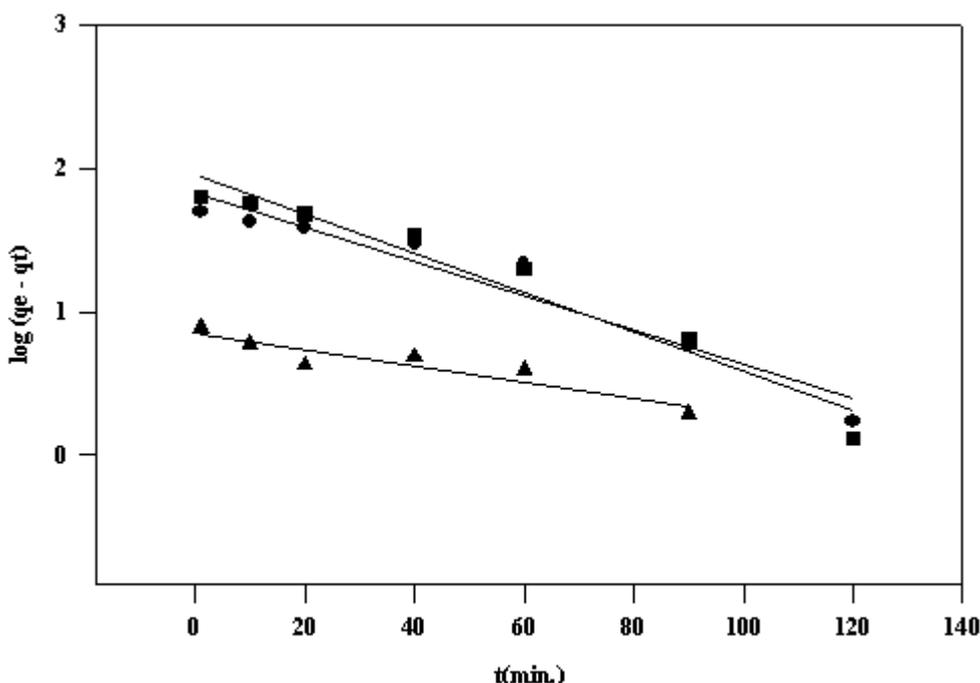


Fig. 14 : Application of the first order kinetic equation for the sorption of:
 ● Co(II), ■ Mn and ▲ Pb species

The new modified ion exchange resin is the synthesized ion exchanger prepared in the current study. For identification of this resin, x-ray diffraction, IR -spectroscopy and electronic microscopy are performed. The CEC as well as the specific surface area are also determined. The resin is found to be more selective for the removal of Co²⁺, Pb²⁺ and Mn²⁺ metal ions from aqueous solutions. the uptake of these metal ions are studied under different parameters including, pH, weight loaded different ion concentrations, and contact time intervals The sorption at equilibrium state are described by the Freundlich and Dubinin and Radushkevich (D-R) isotherm equations and the data fit in a good way with Freundlich and D-R isotherms . the adsorption energy are found to be in the ion exchange reaction ranges. Kinetic analyses are perfectly described by the pseudo-second order kinetic equation.

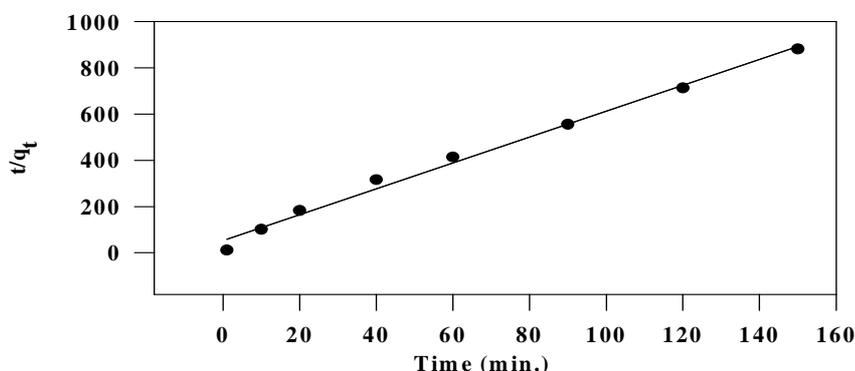


Fig. 15: Pseudo-second-order kinetic model of lead adsorption on prepared ion exchange sorbent

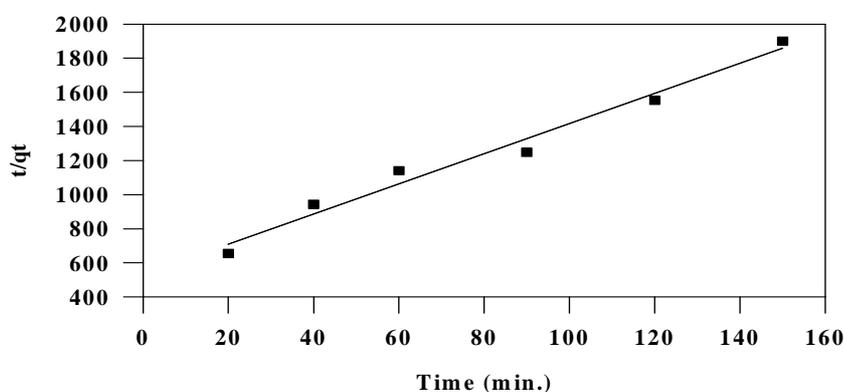


Fig.16: Pseudo-second-order kinetic model plots of lead adsorption on prepared ion exchange resin sorbent

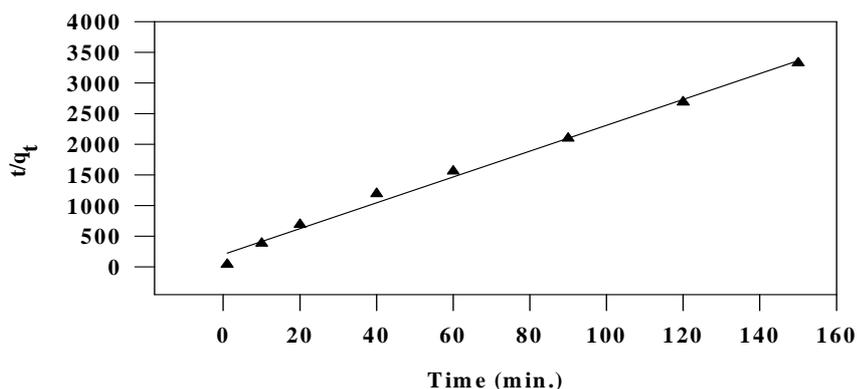


Fig. 17: Pseudo-second-order kinetic model plots of manganese adsorption on prepared ion exchange resin sorbent

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