Colume Chromatographic Separation of Fe (III) at Trace Levels in Various Synthetic Binary Mixtures by Cation – Exchange Resin Impregnated with Neutral Red Dye

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Abstract: A solid phase extraction (SPE) method was developed for the quantitative separation of trace amounts of Fe(III) from synthetic binary mixtures of Pb(II), Cu(II), Ni(II), Mn(II) and Co(II). The cation-exchange resin Lewatite S100 has been modified by adsorption on neutral red dye at pH 3.0 ± 0.5. Binary separations of important metal ions were achieved on the basis of their distribution coefficient (K_d) values when chromatographed with different mobile phases at room temperature. The values of separation factor ( ) and recovery(%) were evaluated by batch technique for predicting the conditions for the possible separations on column in presence of different mobile phase.

1. Introduction:

Much effort is devoted to the determination of heavy metals at trace levels in environmental is one of the targets of analytical chemists[1-3], due to their important roles in our life. There are many difficulties in determining trace amounts of heavy metals in environmental samples by flame atomic absorption spectrometry due to insufficient sensitivity of instrument and/or matrix interferences. In order to achieve detection limits within the range of flame atomic absorption spectrometry. An initial preconcentration step allows lower limits of detection for analytes, as well as the separation of the analytes from its matrix, which may interfere in atomic spectrometric determination[4-8]. Pb(II), Cu(II), Fe(III), Mn(II), Hg(II), Al(III), Cd(II),Zn(II), and Cr(III), are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders[9-10]. They are also common ground water contaminants at industrial and military installations[11]. Iron is a potentially toxic heavy metal, an excess can cause cancer, heart disease, and other illnesses. An excess of iron by destroying vitamin E and oxidizing the unsaturated fats in red blood cells can contribute to hemolytic anemia, in which red cells are so fragile that they breakdown too fast [12]. Meats, grains, eggs, and vegetables naturally contain large amounts of iron. Black olives contain iron, which is used as coloring materials.

The treatment of mixed solutions containing various species may be achieved using conventional treatment depending on the nature of the species present in the solution and the objective of the treatment: separation, concentration, recovery or neutralization. Various separation-preconcentration techniques including solvent extraction [13] ,electro-deposition[14], coprecipitation [15],cloud point extraction[16], membrane filtration[17] and solid phase extraction (SPE) [18,19] have been used for the enrichment and separation of heavy metals at trace levels in various environmental samples including foods and natural waters by the researchers around the world. Solid phase extraction (SPE) is an attractive technique which is widely used, e.g. for cleanup of analytical samples, for purification of various chemicals, and for removal of toxic or valuable substances from aqueous solutions[20]. Solid phase extraction (SPE) is an attractive separation – preconcentratoin technique for heavy metal ions with some important advantages simplicity, Flexibility, economic, rapid, higher enrichment factors, absence of emulsion, time and cost saving [21,22] because of lower consumption of reagents, more importantly environment friendly [23]. Now, several kinds of solid phase extraction (SPE) materials including Lewatite S100 [24], activated carbon[25], ion exchange resins and various polymers have been used as solid phase material [26]. However the ion–exchange resin technique has an advantage of preferentially selecting some metals and rejecting others. It is a well – established technology, particularly in water purification and the concentration and removal of hazardous substances at very low concentration in chemical process industries[27]. This selection is obtained by the introduction of chelating properties into the resin by fixation of specific compounds containing nitrogen, sulphur and oxygen atoms. Lewatite S100 is a

strongly acidic gel-like cation exchange resin with beads of uniform size based on a styrene divinylbenzene copolymer. Its principle characteristics are great chemical and physical stability, good ion-exchange kinetics and high exchange capacity so it can be very suitable for the treatment of electroplating rinse water and to remove heavy metal from water. lewatite S100 resin has many advantage: great selectivity and high efficiencies[24]. The addition of the chelating agent may be carried out by the synthesis of a novel chelation ion exchanger or by impregnation of the resin with a polyelectrtolyte or organic macro-cation. Pyrogallol sulfonic acid [28] enabled the separation and enrichment of Mo^{+6} and Fe^{+3}. Incorporation of the thiol[29] functional group resulted in a chelating resin with high selectivity towards heavy metal ions. Nabi et al. synthesized a variety of chelate – forming resins by incorporating complexing agent such as bromophenol blue[30] eriochrome blackT [31], congored [32] alizarin red [33] and crystal violet [34]. The efficiency of metal separation/preconcentration depends on choice of eluting agent and elution conditions as, various eluting presenting different desorption mechanisms may be used, lowering pH e.g. with mineral acids, causes metal disorption resulting from competition between protons and metal ions for binding sites.

This work was undertaken to develop a novel modified ion exchange resin for separation of Fe(III) from a synthetic binary mixtures. The strong acid – cation exchange resin Lewatite S100 was modified by impregnation in neutral red dye, which might bind to the resin matrix react selectively with metal ions. The analytical applications of the material have explored Fe(III). Under the best conditions of pH, concentration and temperature for modification were selected, the obtained resin was used in batch experiments for the selectively separated Fe(III) ions from a synthetic binary mixture of other heavy metal ions. Two types of treatment were adopted: the sequential retention of ions in the same unit and a retention–elution procedure using chemical reagent. The separation factor ( ) and recovery(%) for ion exchange separation of some metal ions in the presence of different eluents were calculated on the basis of their distribution coefficient (K_d)

2. Experimental
2.1. Resins and solutions

The strong-acid cation exchange resin Lewatite S100 with sulfonic acid-S_3OH group was used in this work. It is kindly obtained from Bayer chemical company Germany. The physical and chemical properties of the reins are listed in Table 1. Prior to use, the resin was washed with HCl (0.1-2.0

mol/dm^3) in sequence remove possible organic and inorganic impurities and convert to hydrogen form. They were washed with deionized water until all chloride ions were removed, and then dried in a vacuum oven at 50°C and left for overnight.

Analytical reagent Fe(III), Pb(III), Cu(II) Ni (II), Mn(II) and Co(II) as nitrates, acetic acid, sod acetate and other inorganic chemicals such as HNO_3 acid were purchased from Merck Co. they were used without further purification. pH was adjusted in the range 3.0 ± 0.5 by adding small amounts of 0.1 mol/dm^3 of HCl or NaOH. This is because a further increase in pH had little, and even negative, effect on metal ion exchange [35].

Table 1. General properties of Lewatite S100 cation exchange resin

Resin	Lewatite S100
Ionic form	Na+
Functional group	Sulfonic acid
pH range	0-14
Structure	Gel type heads
Matrix	Cross linked polystyrene
Bead size	0.315-1.25 mm
Density	~ 1.28 g/ml
Capacity	2.0 eq./L
Storability	2 min-years
Appearance	Light-brown translucent

2.3. Preparation of modified resins

Cation-exchange resins Lewatite S100 (1.0 gm) were impregnate with (20.0 ml) of neutral red (NR) (1000 mg/l) in 100-ml conical flasks for 4h. The resins were separated from the solution by simple filtration. The colour of the Lewatite S100 resins changes from golden yellow to brick red. The treated resins were washed several times with deionized water. Table 2 represents the chemical structure and properties of neutral red. Equilibrium conditions such as concentrations, pH, and adsorption time for neutral red were studied [36].

Table 2: Structure and characteristics of neutral red dye :
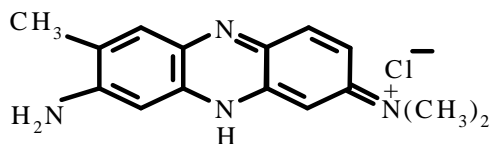
C.I. No	: 50040
Formula	: $C_{15}H_{17}ClN_4$
Molecular weight	: 288.78 g/mol

Appearance   :
    very dark – green powder

λ_{max} : 540 nm

2.3 Batch exchange and elution experiments

In the batch exchange experiments, an aliquot of dry modified resin beads (1.0 gm) and 40 cm^3 of the aqueous solution containing 100 ppm of each metal in 100cm^3 glass stopper for 24h at room temperature. After equilibrium, the resin was separated and the concentrations of metals in the aqueous phase were analyzed by an atomic absorption spectrophotometer (AAS).

The quantitative elution of Fe(III) ions were performed by adding 10.0 gm resin in 100 ml solution containing 100 ppm of Fe(NO$_3$)$_3$ solution was passed through the column at a rate of 1ml/min, resin bed (1.4cm x 12.9 cm). The resin was washed with 50 ml of water and then the Fe(III) was eluted with 200 ml of different eluents. The solvent systems studied are listed in Table 3. In each case the elution rate was 1ml/min and the eluting agent was collected in 10 ml, the free column volume in this work is found to be 13 ml.

Table 3. Solvent systems used for determination of distribution coefficients (K$_d$) of metal ions

Solvent system	Composition (V/V)	Notation
0.05M acetic acid		S_1
0.50 M sodium acetate		S_2
0.05 M acetic acid + 0.050 M sodium acetate	1:1	S_3
0.05 M acetic acid + 1.00 M sodium acetate	1:1	S_4
3MHNO$_3$		S_5

2.4 Apparatus

Thermo Jarrel ASH atomic absorption spectrophotometer (AAS) model (POEMSIII) USA was used to analyze the concentration of metal ion in solution. The pH values of all prepared solutions were measured using pH meter microprocessor, pH meter model (HANNA-pH211) with a combined electro reading to 0.05 pH value.

3. Results and discussion
3.1. Determination of the equilibrium distribution coefficient, (K$_d$)

The distribution coefficient, (K$_d$) is defined as the ratio of the metal ion concentration on the modified resin[NR-Lewatite S100] to that in the aqueous solution and can be used as a valuable tool to study metal ion mobility. High values of distribution coefficient (K$_d$) indicate that the metal has been retained by the solid phase extraction (SPE), while

low values of (K$_d$), indicate that a large fraction of the metal ions remains in solution. The distribution coefficient (K$_d$) was calculated using the following equation [37].

$$K_d = \frac{amount\ of\ metal\ ion\ in\ resin}{amount\ of\ metal\ ion\ in\ solution} \times \frac{v}{m}\ ml/g \qquad (2)$$

Where v is the volume of the solution (ml) and m is the weight of resin(g), K$_d$ values for the metal ions in different solvent systems are presented in Table 4.

It is apparent from the distribution coefficients (K$_d$) given in Table 4, that the modified cation- exchange resin has different selectivity for metal ions, possibly because of the formation of metal complexes with different stability constants[36]. The type of solvent used will also affect the ease of complexation. Studies of the adsorption of different metal ions in diverse solvent systems revealed many interesting features. It was observed from Table 4, that almost all the metal ions expect Fe(III) had low (K$_d$) values in (S$_3$) possibly because of the greater tendency of Fe(III) to complex with[NR-Lewatite S100], the exceptionally high (K$_d$) value for Fe(III) in all solvents (s$_1$–S$_5$) made it possible to separate it from other metal ions. It is interesting to note that (K$_d$) values of the metal ions decrease with increasing sodium acetate content in the mixed sodium acetate-acetic acid system. Where Fe(III) has higher (K$_d$) values compared to other metal ions Pb(II), Cu(II), Ni(II), Mn(II) and Co(II) in sodium acetate – acetic acid (S$_3$) and 3M HNO$_3$ (S$_5$) hence Fe(III) can be separated from other metal ions in the presence of S$_3$ and S$_5$

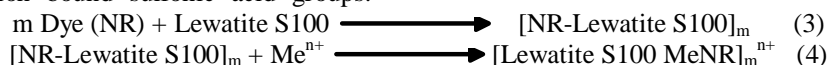**Table 4. Distribution coefficient (K$_d$) for some metal ions in the different solvent systems.**

Metal ion	Distribution coefficient K$_d$ (ml/g)				
	S_1	S_2	S_3	S_4	S_5
Fe(III)	2032.62	1022.11	4707.69	2358.72	2.46
Pb(II)	5.20	4.89	7.31	1.25	0.36
Cu(II)	20.73	3.77	6.14	2.75	1.32
Ni(II)	500.02	200.71	2.39	0.47	1.35
Mn(II)	208.71	78.71	36.66	21.71	1.38
Co(II)	400.11	200.23	2.10	1.98	1.06

3.2. Quantitative separation of metal ions

Separation of the metal ions was performed by an elution technique. Modified resin (2g) was packed into a glass column of (1.4 cm x 12.9 cm), with a glass wool support at the end and washed 2-3 times with deionized water. Binary solutions of the metal ions were prepared by mixing100 ppm solutions of each ion. The binary mixture was them poured on to top of the column and the solution was left to flow 1ml/min through the column until a small amount remained above the surface of the resin. The

column was then rinsed with deionized water. The effluent collected was recycled through the column to ensure complete absorption of metal ions. The metal ions were then eluted with an appropriate mobile phase, the effluent was collected in 10 ml fractions. The metal ion content of each 10 ml fraction was determined using atomic absorption spectra (AAS).

An effective way of separating solute particles and capable of extracting positively charged ions is ion- exchange technique. Ion exchange technique is a widely used method for the separation and pre-concentration of inorganic ions. In ion exchange, ions of positive charge and negative charge ions from an aqueous solution replaced of the same charge initially in the solid, cation exchange resins lewatite S100 cation bound sulfonic acid groups.

$$m \, Dye \, (NR) + Lewatite \, S100 \longrightarrow [NR\text{-}Lewatite \, S100]_m \quad (3)$$
$$[NR\text{-}Lewatite \, S100]_m + Me^{n+} \longrightarrow [Lewatite \, S100 \, MeNR]_m^{n+} \quad (4)$$

The loading percentages of the metal ions [39] were calculated from the following equation as shown in Table 5.

$$L \, \% = \frac{m \, equiv. \, of \, metal \, ions \, / \, g \, of \, resin}{m \, equiv. \, of \, metal \, ions \, initially \, taken} \times 100 \quad (5)$$

The quantitative separation of Fe (III) from other heavy metals Pb(II), Cu(II), Ni(II), Mn(II), and Co(II) has been achieved. The effluent fractions were collected in 10 ml portion and analyses for the metal ions inside it using atomic absorption spectrophotometer (AAs). Fe (III))was taken up weakly by the resin in comparison with other ions and hence it was eluted first, while strongly adsorbed ions were eluted later with suitable eluent. The separation of Fe(III) from other metal ions are based on the fact that 0.05M acetic acid – 0.5M sodium acetate is a good elunet for Fe(III) but fails to elute the other cations.

Table 5. Distribution coefficient (K_d) and loading percentage (L%) of some metal ions in the presence of different eluents.

Eluting agent					
Metal ion	S_3		S_4		S_5	
	K_d	L%	K_d	L%	K_d	L%
Fe(III)	4707.69	244.80	2358.72	239.82	2.46	6.25
Pb(II)	7.31	17.05	1.25	3.10	0.36	0.90
Cu(II)	6.14	14.47	3.75	6.70	1.32	3.26
Ni(II)	2.39	5.85	0.47	1.17	1.35	3.32
Mn(II)	36.66	52.62	21.71	44.60	1.38	3.40
Co(II)	2.10	5.15	1.98	4.87	1.06	23.45

The separation factors ( ), were calculated from the following equation [40]

Certain general rules for cation exchange are : (i) the exchange prefers ions of high charge, (ii) ions of small hydrated volume are preferred and (iii) ions, which interact strongly with the functional groups of the exchangers are preferred [38].

Neutral red (NR), which contains two aromatic rings, was attached to the poly styrene skeleton by physical adsorption π-π dispersion forces arising from the aromatic nature of resin and neutral red (NR) seem to be responsible for this adsorption. The presence of two nitrogen donor atoms of the neutral red (NR) facilitates its selective interaction with metal ions [36]. Hence the metal ion undergoes autocomplex formation in[NR-Lewatite S100] can be shown as:

$$\alpha = \frac{K_d A}{K_d B} \quad (6)$$

A and B are different metal ions pairs estimated.

Table 6 shows that the most effective separation of Fe(III)–Ni(II) mixture is obtained with 0.05 M acetic acid and 0.5M sodium acetate, with very large separation factor ($\alpha \dfrac{Fe(III)}{Ni(II)} = 4997.29$)

followed by the elution of other ions. In Fe(III)–Ni(II) and Fe(III)–Co(II) binary mixture, these metal ions have nearly similar distribution coefficients (K_d) and high separation factors ( ) in the presence of 0.05M acetic acid –0.5M sodium acetate for these reasons no separation is possible.

3.3. Selective separation of Fe(III) from other metals in a binary synthetic mixture

For selective separation of Fe(III) from a mixture prepared by mixing a known volume of the mixture of other metal ions a synthetic mixture was poured on the column using the same procedure as described for binary separation of metal ions, Pb(II), Cu(II), Ni(II), Mn(II) and Co(II) were eluted together by use of 0.05 M acetic acid – 0.5M sodium acetate. Fe(III) was strongly retained by the modified ion-exchange resin and was eluted with 3.00 M nitric acid

solution. The total volume of an eluent used for complete removal of a particular metal ion and the quantities separated are given in Table 8. Also the recovery % of some metal ions in the presence of different eluent using modified cation exchange resin[NR-Lewatite S100] are listed in Table 7. The recovery % was calculated from the following equation.

$$\text{Recovery \%} = \frac{[M]^{n+}\ \text{eluted}}{[M]^{n+}\ \text{fixed}}\ 100 \qquad (7)$$

Selective separation of Fe(III) ion from a synthetic mixture of Pb(II), Cu(II), Ni(II), Mn(II), and Co(II) are presented in Table 8.

3.4. Effect of the sample volume on the recoveries

The effect of the sample volume on the metal sorption on modified [NR-Lewatite S100] ml volumes through column at a 1 ml/min flow rate. The results were given in Figs. 1-5. The percent sorption decreased for the analyste above 60ml. The recoveries of analytes decrease probably due to the excess analytes loaded over the column capacity with increasing sample volume.

Table 6. Separation factors ( ) of some metal ions in the presence of different solvent systems using(NR-lewatite S100)

Cations	Separation factor	Eluting agent
Fe(III)-Pb(II)	643.22	0.05M acetic acid+1.00 M sodium acetate
Fe(III)-Pb(II)	1879.46	0.05M acetic acid+0.5 M sodium acetate
Fe(III)-Cu(II)	857.72	0.05M acetic acid+ 0.5 M sodium acetate
Fe(III)-Ni(II)	4997.29	0.05M acetic acid+0.5 M sodium acetate
Fe(III)-Mn(II)	108.65	0.05M acetic acid+0.5 M sodium acetate
Fe(III)-Co(II)	1185.88	0.05M acetic acid+0.5 M sodium acetate

Table 7. Recovery % of Fe(III) from a binary mixture in the presence of different elunet using (NR-lewatite S100).

Binary mixture	Amount loaded (ppm)	Amount found (ppm)	Recovery (%)	Volume of eluent (mL)	Eluent used
Fe(III)	9.46	9.24	97.67	200	3M Nitric acid (HNO_3)
Pb(II)	9.96	9.52	95.58	200	0.05M acetic acid+ 0.5 M sodium acetate
Fe(III)	9.63	9.33	96.88	200	3M Nitric acid (HNO_3)
Cu(II)	9.95	9.34	93.87	200	0.05M acetic acid+ 0.5 M sodium acetate
Fe(III)	10.00	9.89	98.90	200	3M Nitric acid (HNO_3)
Ni(II)	9.95	9.09	91.35	200	0.05M acetic acid+ 0.5 M sodium acetate
Fe(III)	10.00	9.89	99.80	200	3M Nitric acid (HNO_3)
Mn(II)	9.95	8.92	89.65	200	0.05M acetic acid+ 0.5 M sodium acetate
Fe(III)	9.99	9.82	98.29	200	3M Nitric acid (HNO_3)
Co(II)	9.99	9.70	97.09	200	0.05M acetic acid+ 0.5 M sodium acetate

Table 8. Selective separation of Fe(III) from a binary mixtures using (NR-lewatite S100).

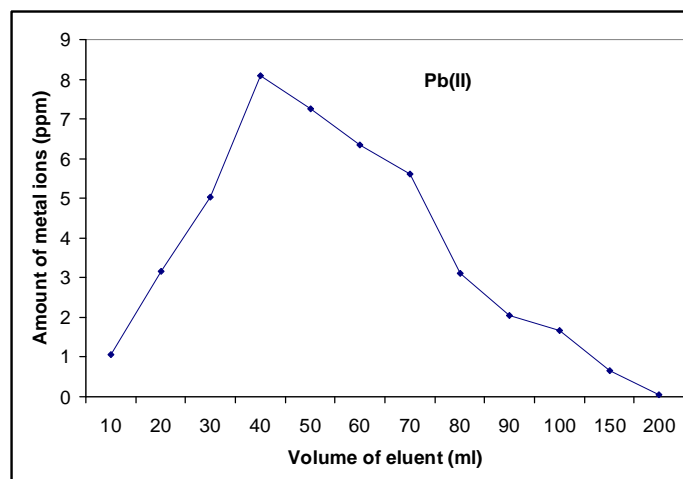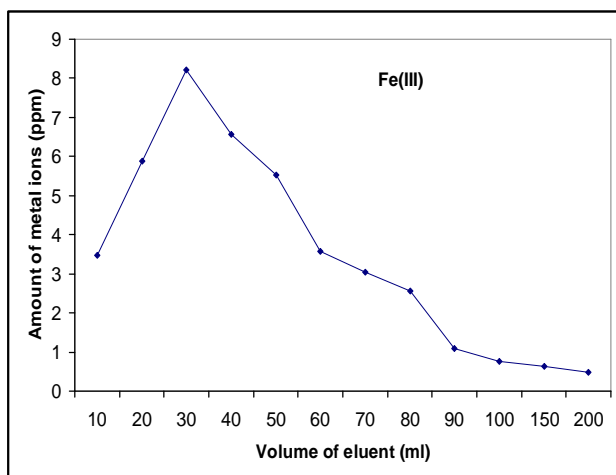| Metal ion	Amount of Fe(III) loaded (ppm)	Amount of Fe(III) found (ppm)	Recovery %	Eluent used	Volume of elunet (ml)
Fe(III)-Pb(II)	9.46	9.24	97.67	3.0 M nitric acid	200
Fe(III)-Cu(II)	9.63	9.33	96.88	3.0 M nitric acid	200
Fe(III)-Ni(II)	10.00	9.89	98.90	3.0 M nitric acid	200
Fe(III)-Mn(II)	10.00	9.98	99.80	3.0 M nitric acid	200
Fe(III)-Co(II)	9.99	9.82	98.29	3.0 M nitric acid	200

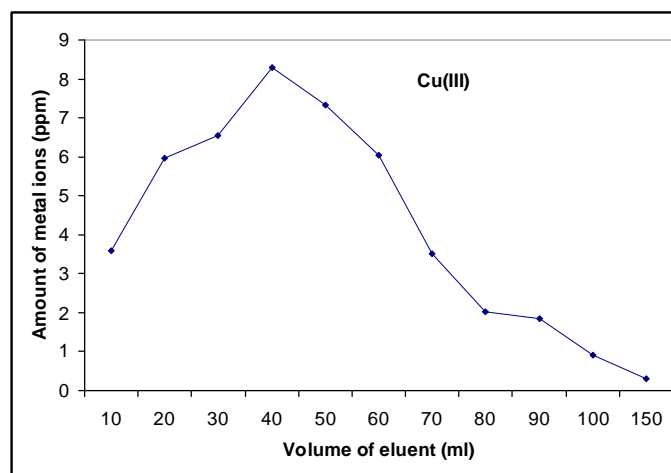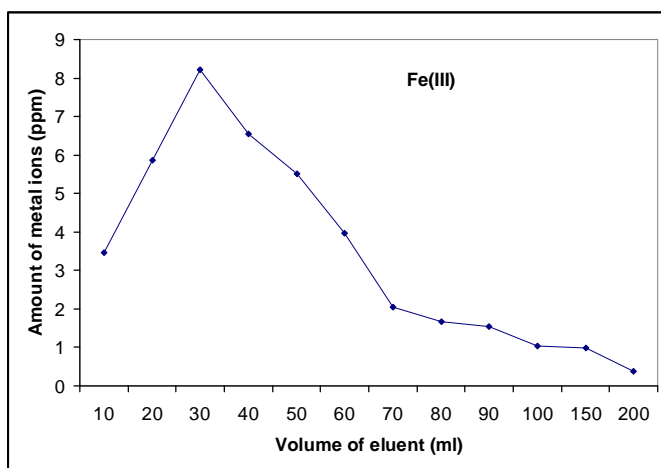**Fig. 1. Elutions curves for separation of Fe(III) – Pb(II) binary mixtures using (NR-lewatite S100).**

Fig. 2. Elutions curves for separation of Fe(III) – Cu(II) binary mixtures using (NR-lewatite S100).
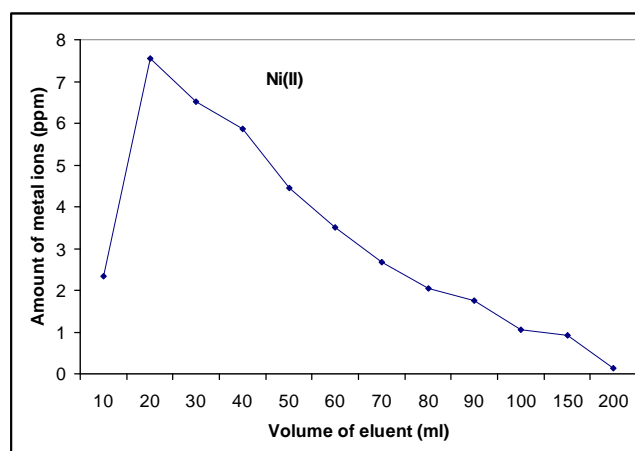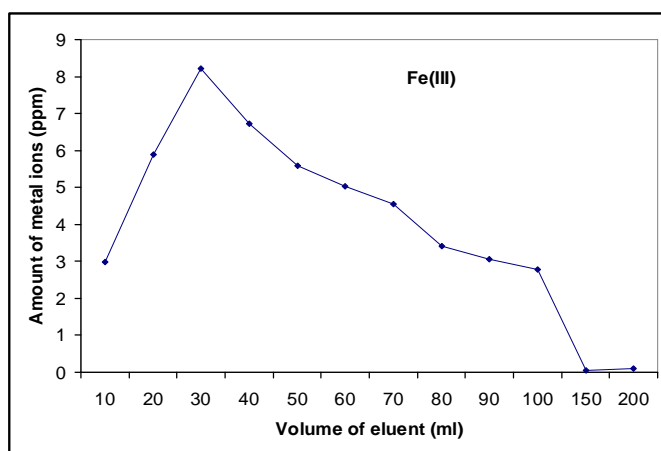

Fig. 3. Elutions curves for separation of Fe(III) – Ni(II) binary mixtures using (NR-lewatite S100).
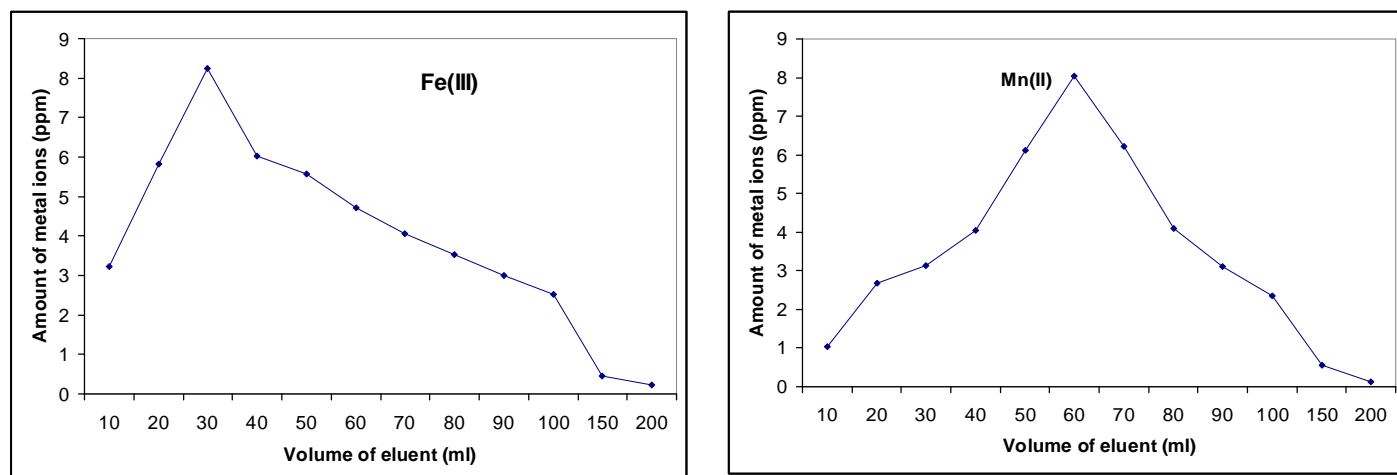
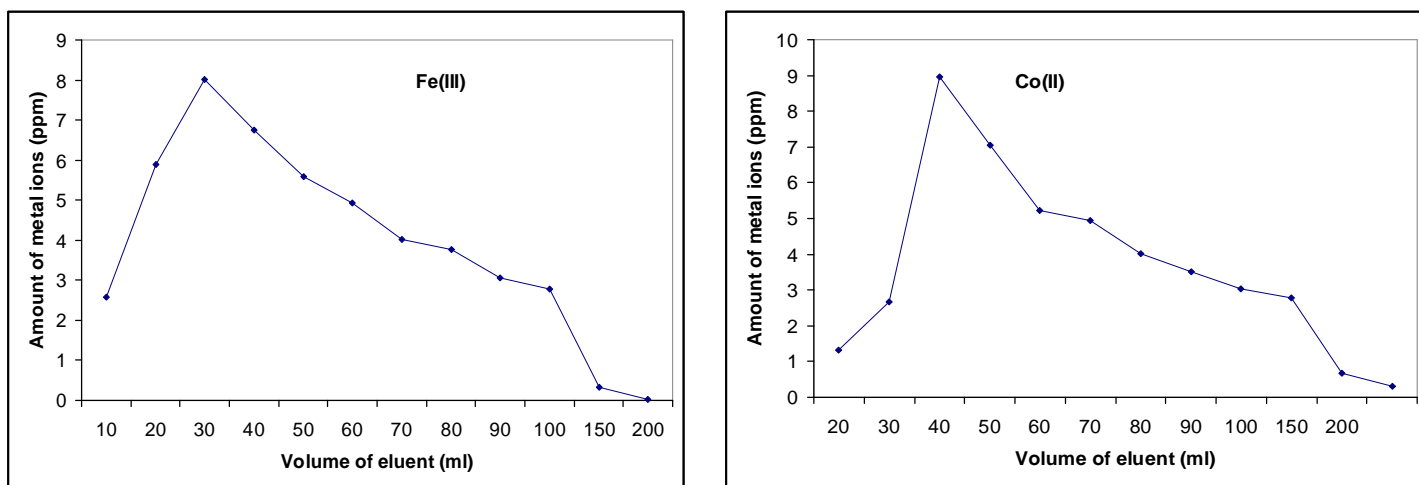**Fig. 4. Elutions curves for separation of Fe(III) – Mn(II) binary mixtures using (NR-lewatite S100).**

Fig. 5. Elutions curves for separation of Fe(III) – Co(II) binary mixtures using (NR-lewatite S100).

4. Conclusion

The present investigation shows that neutral red loaded with cation- exchange resin (NR-lewatite S100) has differential selectively for metal ions. It can be used as a packing material in column chromatography and for preconcentration and recover of Fe(III) from binary synthetic mixtures. Batch method and column elution were done for the separation of Fe(III) from binary mixture of Fe(III)-Pb(II), Fe(II), –Cu(II), Fe(III)- Ni(II), Fe(III)- Mn(III) and Fe(III)-Co(II), The described methods provide a simple, fast and economic means for separating Fe(III) quantitative from Pb(II), Cu(II), Ni(II), Mn(II), Co(II).

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