# 3-RESULTS AND DISCUSSION

This chapter contains the data obtained from the adsorption (uptake) and desorption experiments conducted under various conditions to study the relation between the uptake of the various elements individually on the natural samples used and their desorption as well as similar results for a mixture of selected elements. Data of the trials for separating the elements from the raw materials used and the conditions affecting this separation is also discussed. Data obtained for the characterization of pollution of a certain type of wastewater is also given and discussed(131).

## 3.1. Data of the determination of the V/m ratio:

The ratio of the volume of the aqueous phase to the mass of straw V/m is a very important parameter in the adsorption process. Effect of V/m value on adsorption of Cr(VI) on different straw and sugarcane residue samples has been studied in sulfuric acid media. Table (9) shows that Cr(VI) ions in sulfuric acid solution at pH=1 have the highest uptake percent at V/m ratio=100 ml/g for two straw and the sugarcane samples.

Table (9): Adsorption of Cr(VI) on R.S, M.S& S.C from sulfuric acid solution at pH=1 using different V/m values.

| Sample | V/m= 33.33 ml/g Uptake % of Cr(VI) | V/m=100 ml/g Uptake % of Cr(VI) |
|---|---|---|
| S.C | 74.1 | 86.86 |
| R.S | 75.7 | 88.56 |
| M.S | 80.9 | 92 |

Thus the V/m ratio chosen is (10/0.1), i.e. 100ml/g. This ratio was maintained unvaried for all the conducted experiments and also the diameter of straw particle size of 0.63mm was throughout the present experimental work.

### 3.2. Determination of moisture content:

Data of the moisture content as percentage for the three straw samples and the sugarcane residue is given in table (10).

Table (10) Moisture content of the materials used.

| Sample | % Moisture content |
|---|---|
| S.C | 17.7 |
| M.S | 9.66 |
| W.S | 8.14 |
| R.S | 7.79 |

It is obvious from this table the moisture content is highest in S.C residue followed by M.S, W.S and then R.S. The value of the sugarcane is almost twice that of the other straw. This means that the water content in S.C residue is high and this high water content will undoubtedly have some impact on the capacity of S.C residue for adsorpting certain elements in comparison to the rest of the used straw.

### 3.3. Results on the sorption studies of Cr(VI):

The factors affecting adsorption of chromium on straw and sugarcane samples are the pH, contact time and element concentration.

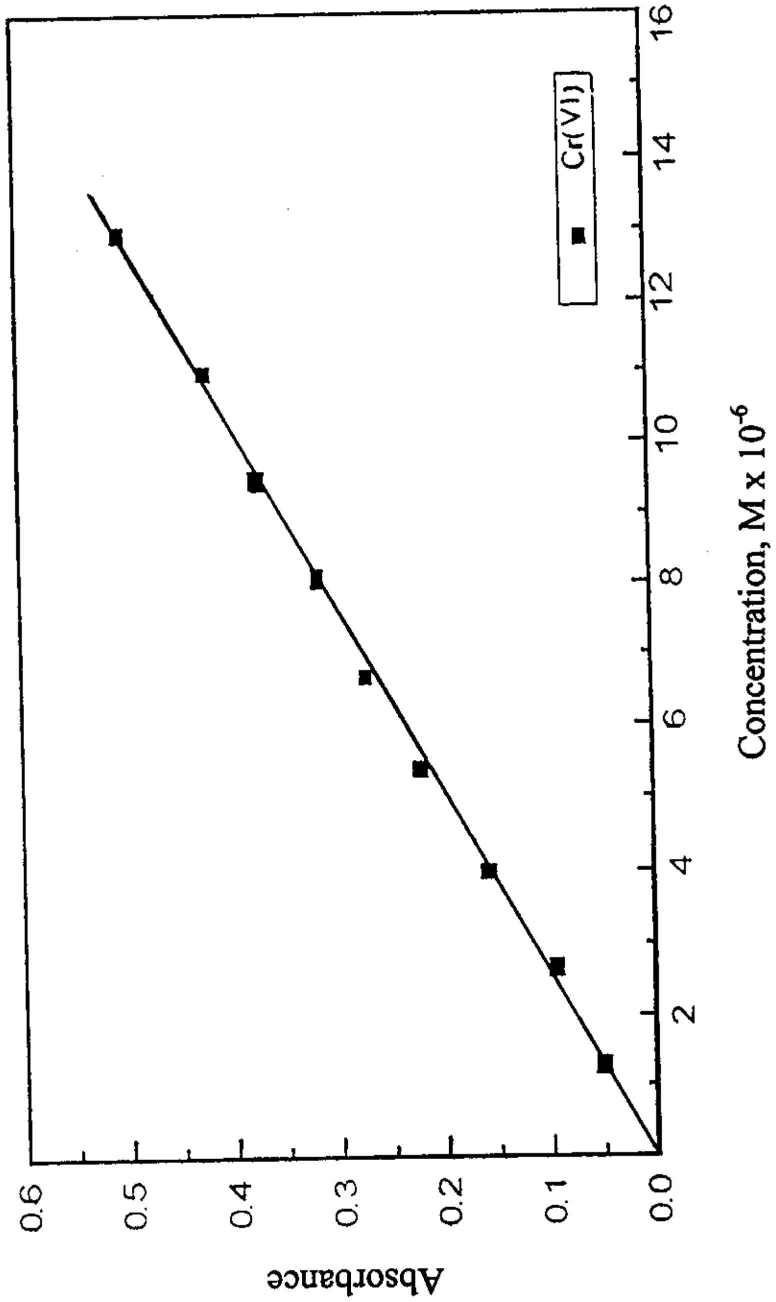

Fig.(1) Calibration curve for Cr(VI) using diphenylcarbazide Dye, at wave length = 540 nm.

In such experiments as the uptake percent was determined by measuring Cr spectrophotometrically by following its absorbance in visible region, it is essential to pre-construct a calibration curve showing the relationship between absorbance and the element concentration, as given in Fig.(1). From this figure the concentration range which obeys Beer's Lambert Law was chosen to study the amount of Cr(VI) adsorbed on straw as a function of various variables mentioned before.

### 3.3.1. Effect of pH:

The results of the effect of varying the pH of the aqueous phase on the adsorption of chromium on sugarcane residue and different straw samples are shown in Figs.(2a,2b). As shown in these figures, at pH=1, 100% adsorption of chromium is observed (i.e. complete adsorption). With increasing pH values, the adsorption of Cr(VI) decreases sharply till pH=4. This sharp decrease in the adsorption of Cr(VI) with decreasing the acidity is to be explained with possible changes that may occur for the Cr ion with increasing the pH of the aqueous solution giving rise to non absorbable Cr species. Sugarcane residue shows slightly higher ability to adsorb Cr(VI) in pH range 3-4 than the other straw samples. The decrease of adsorption of Cr(VI) with decreasing the acidity is likely explainable by reduction of Cr(VI) to Cr(III)(132).

### 3.3.2. Effect of contact time:

Figs.(3a,3b) show the effect of contact time on adsorption of Cr(VI) from sulfuric acid media at pH=1. The uptake percent of Cr(VI) reaches 100% for rice and maize straw samples after shaking time of 2h. While its uptake on sugarcane residue and wheat straw samples reaches

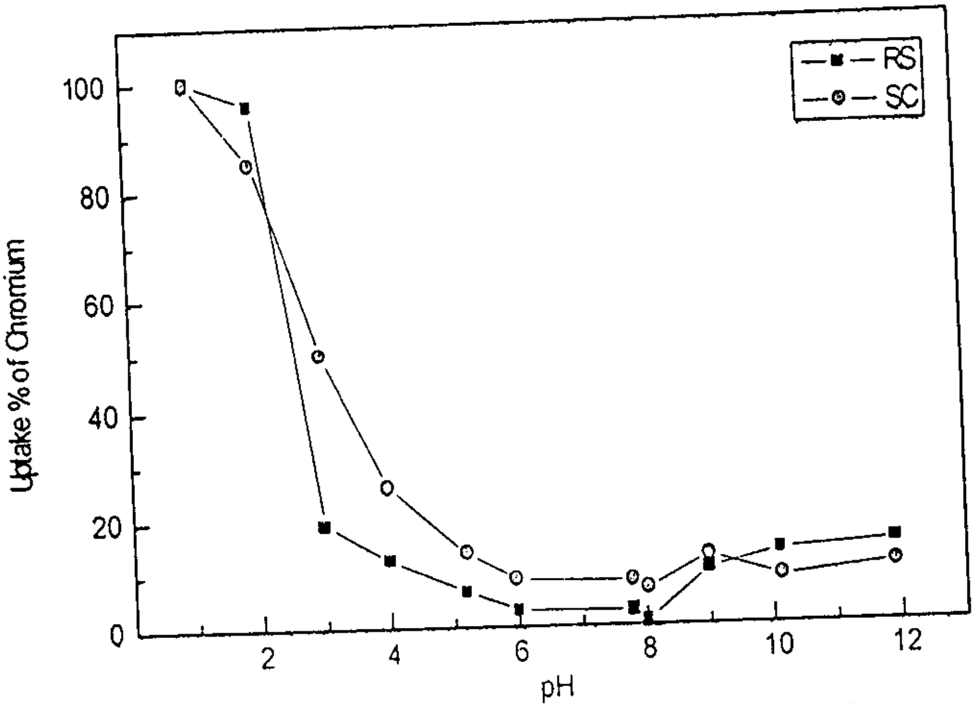

Fig.(2a) Effect of pH variation on the adsorption of chromium by rice straw and sugarcane residue samples.

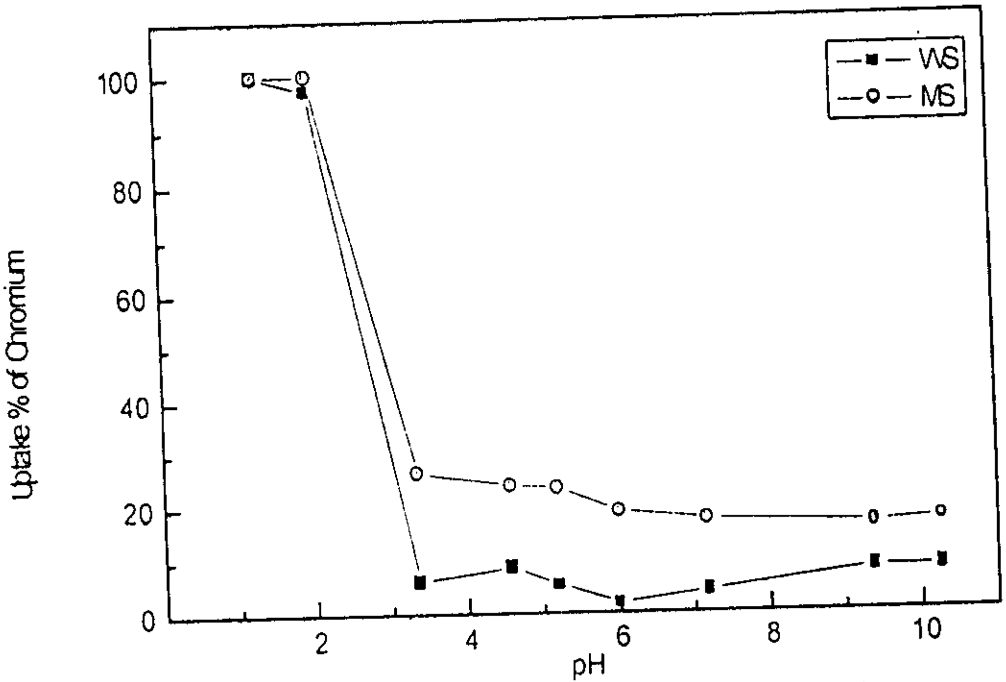

Fig.(2b) Effect of pH variation on adsorption of chromium by wheat and maize straw samples.

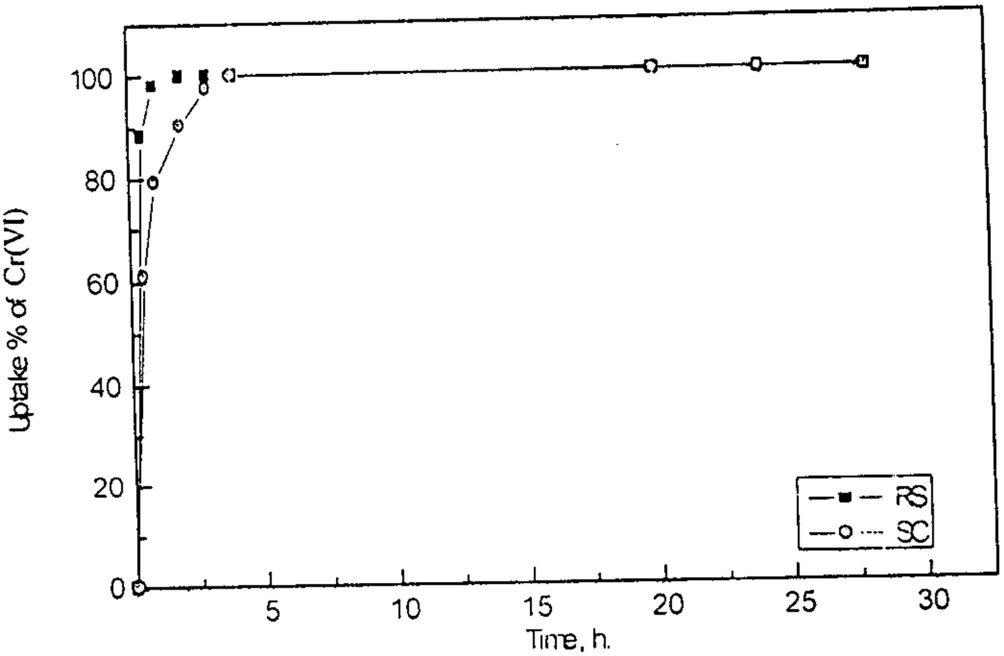

Fig.(3a) Effect of contact time on adsorption of Cr(VI) from sulfuric acid solution by rice straw and sugarcane residue samples at pH=1

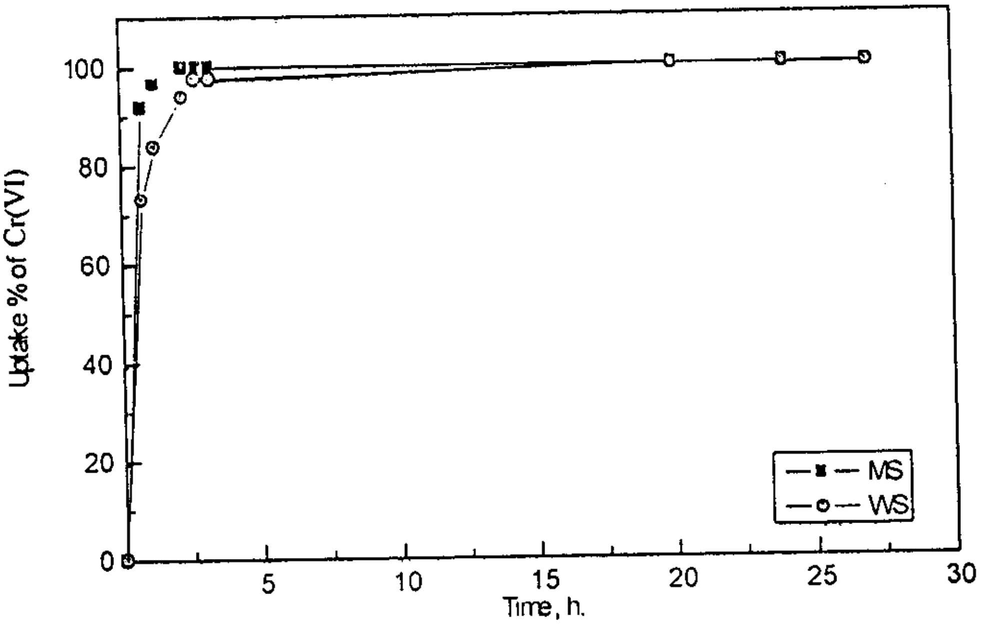

Fig.(3b) Effect of contact time on adsorption of Cr(VI) from sulfuric acid solution by maize and wheat straw samples at pH=1.

100% after 3h. shaking time. So, equilibration time of 3h. for all straw samples was applied for the rest of the experiments conducted in this work.

### 3.3.3. Effect of ion concentration:

Adsorption isotherm of Cr(VI) is carried out using different concentrations of Cr(VI) in sulfuric acid medium of pH=1 on rice straw sample. The amount of Cr(VI) adsorbed per gram (X/m) in meq.g$^{-1}$ is plotted against Cr(VI) concentration [C] on logarithmic scale, Fig.(4). The plot in this figure gives a straight line of slope=1. This linearity of the isotherm means that the adsorption process follows Freundlich isotherm. This means that the adsorption of Cr(VI) cation on straw and sugarcane residue samples takes place through the formation of a single monolayer of sorbed ionic species(118). This finding agrees with that published for the adsorption of various metal ions on cellulose(119), and wood powder(80,120).

The Freundlich isotherm is represented by the equation:

$$X/m = kC^{1/n}$$

$$\text{Log } X/m = \text{Log } k + 1/n \text{ Log } C$$

Where, k and 1/n are empirical constants depending on the nature of both aqueous and solid phases used at fixed temperature.

### 3.3.4. Desorption studies of Cr(VI):

Desorption of Cr(VI) was studied from the different straw and sugarcane residue samples using a cation similar in radius.

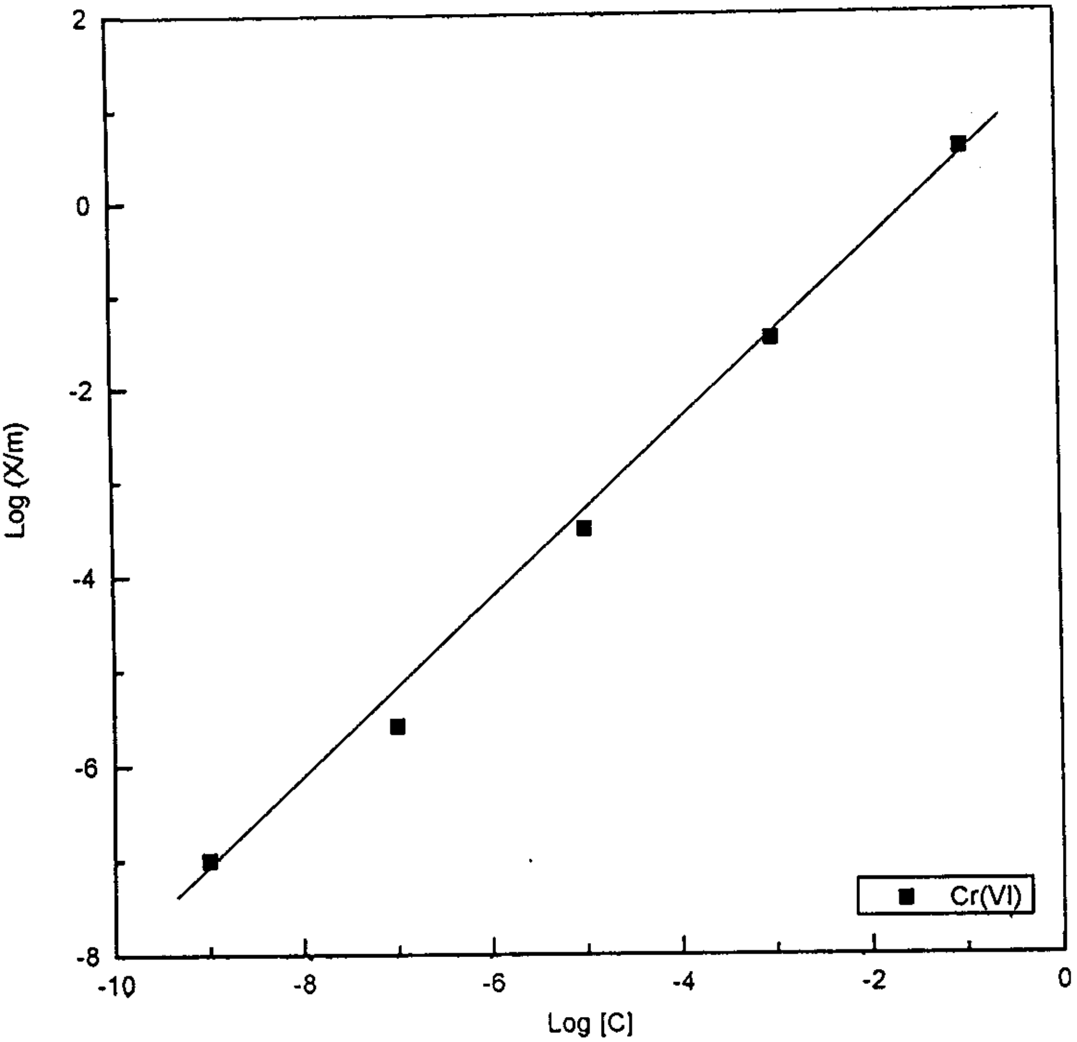

Fig.(4) Effect of chromium concentration on adsorption of Cr(VI) by rice straw sample from sulfuric acid solution at pH=1

0.2M. $Fe(NO_3)_3$ was used as eluent for this purpose. From the data shown in Fig.(5), it is observed that 29% & 22.8%& 15.35% and 20.33% of Cr(VI) was released from S.C, R.S, W.S and M.S samples respectively after 3h. shaking time and these percentages decreased to 9%& 8.4%& 9% and 7.58% respectively when leaving the phases in contact with shaking for more than 24h. this means that through this period of contact time, the amount of Cr(VI) is readsorbed again on different straw and sugarcane residue samples. But when using 0.1M $Fe(NO_3)_3$, it indicated that desorption % of Cr(VI) from S.C, R.S, W.S and M.S is 20.9%& 18.6%& 18.8% and 16.75% respectively. Studying the desorption of Cr(VI) from different straw and sugarcane samples using distilled $H_2O$& different concentration of $Y(NO_3)_3$ [$10^{-2}$, $10^{-3}$,$10^{-4}$M] and $10^{-1}$M $Al(NO_3)_3$ have been tested. The data of such experiments shows that the percent of Cr(VI) eluted by different concentration of $Y(NO_3)_3$ is very low [i.e., Cr(VI) stayed adsorbed on the straw used non affected by the addition of $Y(NO_3)_3$], Fig.(6). Also for using distilled $H_2O$ and $10^{-1}$M $Al(NO_3)_3$ as eluents. It is observed that no desorption is achieved in this case. Which means that $H_2O$ is not suitable as leaching agent for Cr(VI) adsorbed on the straw used. This poor elution is probably a result of interaction between the metal ion in the aqueous phase and some or all of the components of straw. Such interaction is not easily attacked by $H_2O$.This water resistance makes the straw used to be successfully used in nuclear waste management and storage due to the immobilization of the adsorbed element to the surrounding environment.

### 3.4. Studies of Pb(II):

In such studies the amount of lead in the aqueous solution was measured spectrophotometrically(133), by measuring the absorbance at wavelength of 430nm following the calibration curve, Fig.(7).

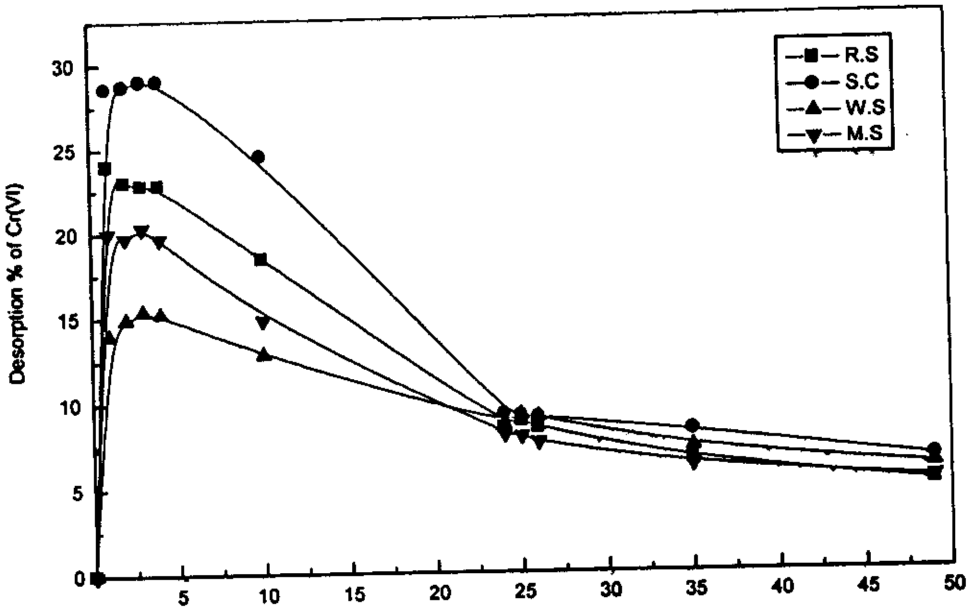

Fig.(5) Effect of contact time on desorption of Cr(VI) from R.S, W.S, M.S& S.C samples at wavelength=540nm. using 0.2M Fe($NO_3$)$_3$.

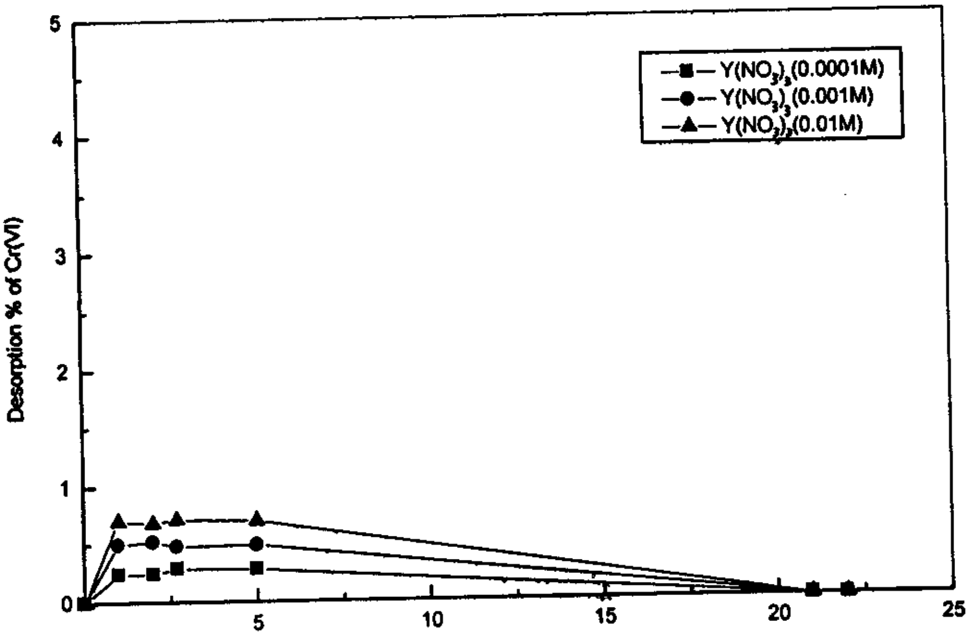

Fig.(6) Effect of contact time on desorption of Cr(VI)from R.S using different concentrations of Y($NO_3$)$_3$.

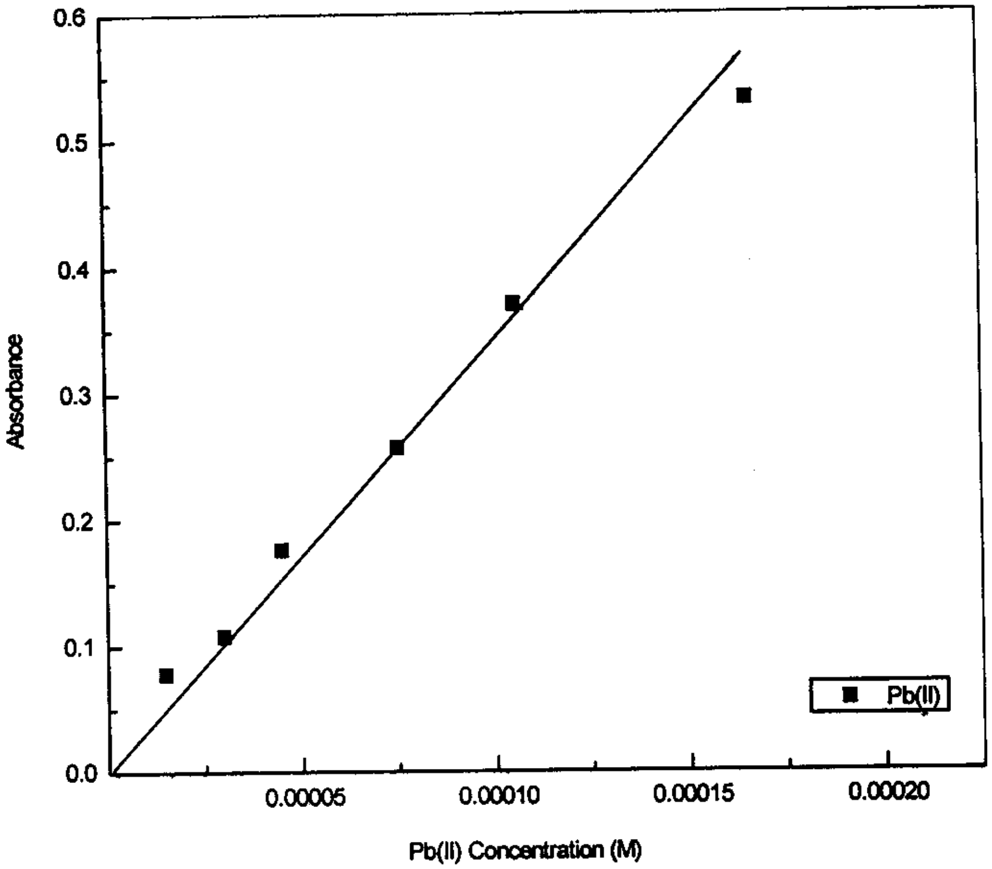

Fig.(7) Calibration curve for pb(II) from nitrate solution at wave length = 430 nm.

### 3.4.1. Effect of pH:

Nitrate solutions of different pH values (1.5-8) were in these experiments. The uptake of Pb(II) on sugarcane is represented against the pH as shown in Fig.(8). In this figure, 90% adsorption of Pb(II) is achieved at pH=5 using initial lead concentration of 10ppm. And this value increases to 97% at pH=5 with increasing initial lead concentration to 100ppm. From this figure, it is observed that, the sorption of Pb(II) cations is low at the acidic pH range and increases to the maximum value with increasing pH values to nearly neutral range. Where, the maximum sorption of Pb(II) is achieved at pH=5. With further increase in the pH values, the adsorbability decreases gradually with increasing pH of the solution phase containing Pb ion. The pH where maximum sorption takes place was chosen to obtain the element in its soluble cationic form ($M^{n+}$). The adsorption of cations is likely to be indicated as a displacement process of the hydrogen ions from non-dissociated surface groups of the adsorbent. Lead forms several hydrolysis products(134) that exist under widely varying conditions. At pH above 6 formation of the hydrolysis products occur in the dilute solutions(135). So, the decrease in adsorption of Pb(II) noted at alkaline pH ranges, is probably due to the formation of hydrolyzed species (as: $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$) having a net +ve charge and weakly sorbed. Similar results were reported for sorption of lead on acrylonitrle- charcoal composite by Kabil et al.(136) and on rice husk by Khalid et al.(137).

### 3.4.2. Effect of contact time:

The effect of contact time on the adsorption of Pb (II) on different straw and sugarcane samples from nitrate solution at pH = 5 is represented in Fig.(9). This figure shows that the uptake percentage of Pb(II) reaches a maximum value of 97% for all the studied samples after a shaking time of 1hour. There is no variation observed for Pb(II) adsorption with increasing the shaking time. So, an equilibrium time of 1hour for all the studied samples is accepted for the rest of the work.

### 3.4.3. Effect of ion concentration:

The adsorption isotherm of Pb(II) was carried out using different concentrations of Pb(II) in nitrate solution on rice straw sample. The amount of Pb(II) adsorbed per gram (X/m) in meq.g$^{-1}$ is plotted against the Pb(II) concentration [C] on logarithmic scale, Fig.(10). The plot in this figure gives a straight line of slope ~ 0.7. this linearity of the isotherm means that the adsorption process follows the Freundlich isotherm. The Freundlich equation used here is that used earlier for Cr(VI). The isotherm model constants were determined at room temperature from the slope (1/n), and intercept, Log k of the straight line in Fig.(10). This means that the adsorption of Pb(II) cation on rice straw sample takes place through the formation of a single monolayer of sorbed ionic species(118). Similar results were reported(138) for the sorption of lead on poly(methyl methacrylate) and also on rice husk by Khalid et al.(137).

### 3.4.4. Effect of competing ion concentration:

Fig.(11) shows the effect of competing ion concentration on the adsorption of Pb(II) on different straw and sugarcane samples at pH=5. Different concentrations of Ni(II) ion are used for competing with Pb(II) adsorption on the studied samples. It is observed that with increasing Ni(II) concentration the adsorption of Pb(II) decreases.

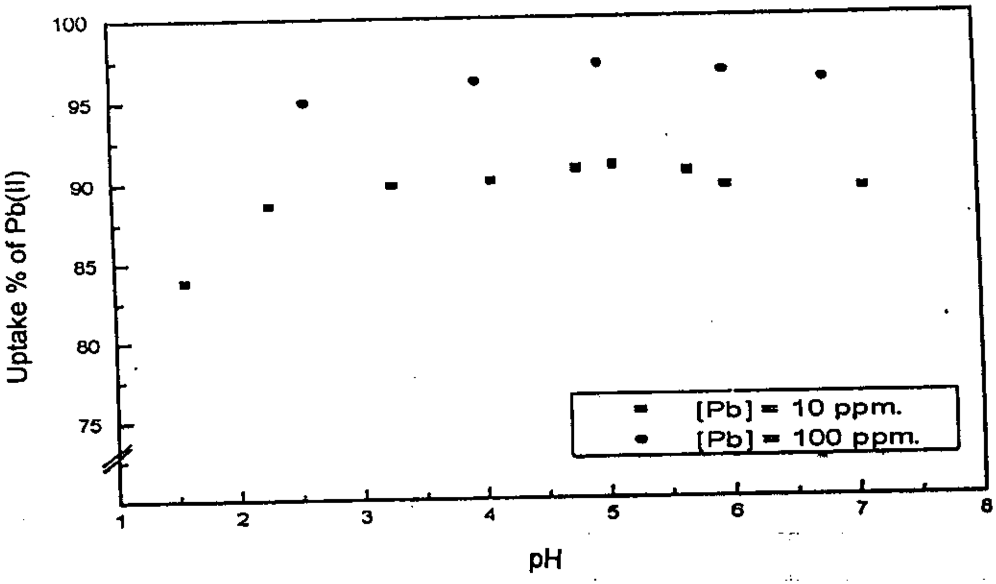

Fig.(8) Effect of pH on adsorption of Pb(II) on sugarcane residue sample.

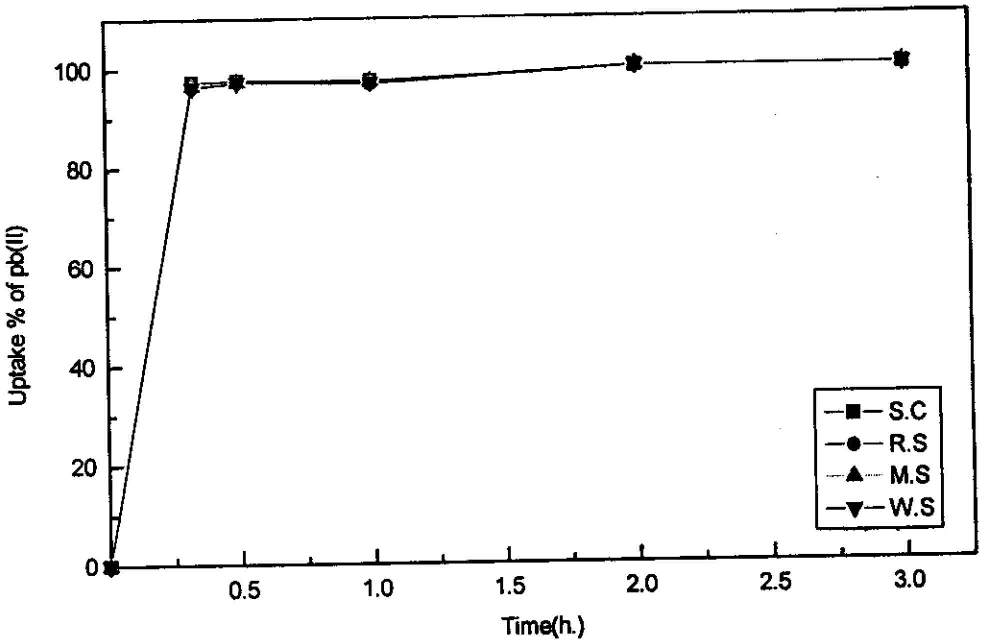

Fig.(9) Effect of contact time on adsorption of pb(II) on different straw and sugarcane residue samples

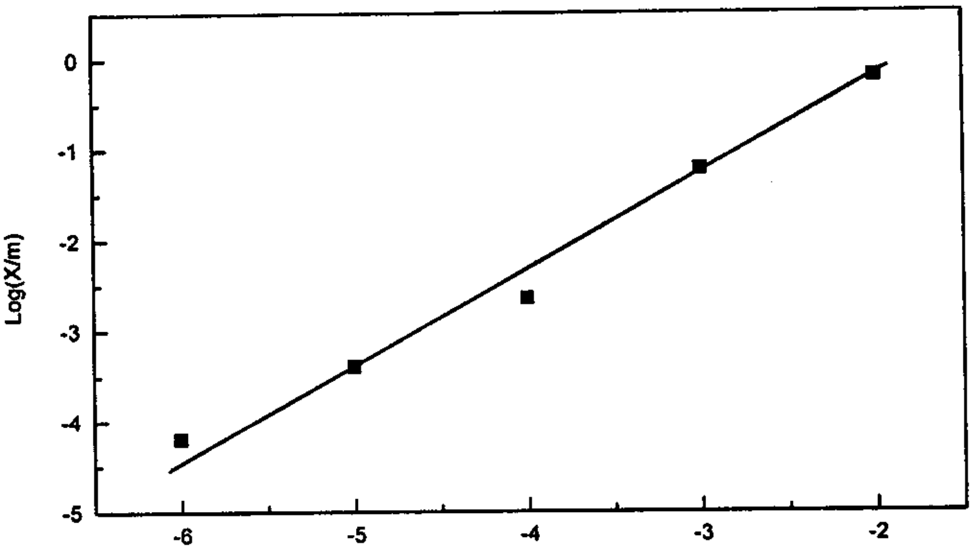

Fig.(10) Effect of lead ion concentration on adsorption of pb(II) on rice straw sample.

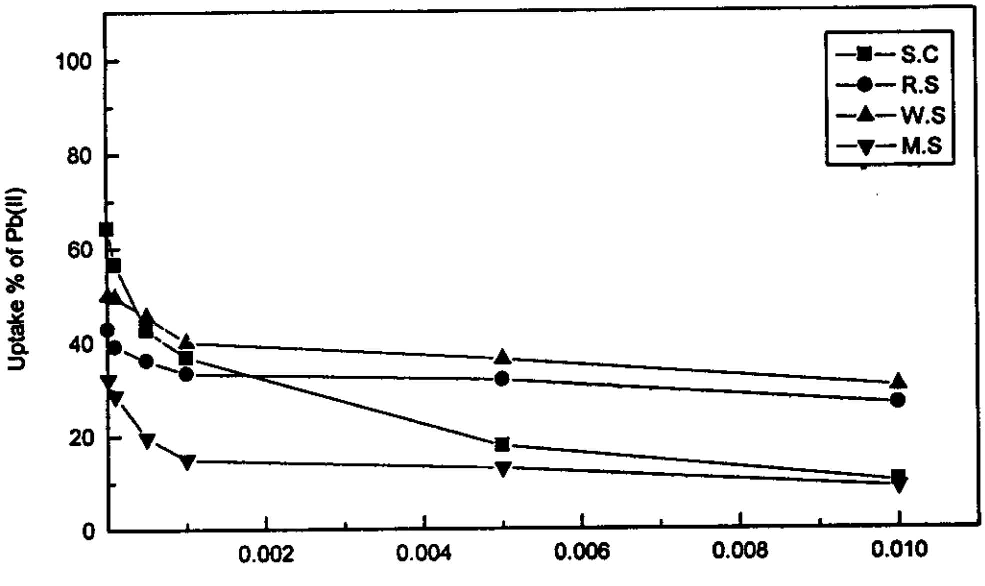

Fig.(11) Effect of Ni(II) ion concentration on adsorption of pb(II) on different straw and sugarcane samples at pH=5.

It should be mentioned here that the ionic radius of Pb(II) and Ni(II) are very close to each other. This similarity may affect the sorption of Pb(II) on the studied samples when Ni(II) is present in the same solution.

### 3.4.5. Desorption studies of Pb(II):

Results of the effect of contact time on desorption of Pb(II) from different straw and sugarcane residue samples using different concentrations of similar cation, ($Mn^{2+}$) are shown in Figs.(12-15). It is obvious from Fig.(12) that desorption of Pb(II) increases with increasing the $MnCl_2$ concentration. Maximum desorption from sugarcane reaches 90% using $10^{-1}$M $MnCl_2$ solution. While using $10^{-3}$M of $MnCl_2$ gives desorption of only 25% of Pb(II) loaded on the sugarcane residue sample. Also, 90% of pb(II) is leached (desorped) from rice straw sample using $10^{-1}$M of $MnCl_2$ solution, as shown in Fig.(13). Maximum desorption of Pb(II) from wheat and maize straw samples reaches 75% using $10^{-1}$M of $MnCl_2$ solution, as shown in Figs.(14and15). And all these desorption values occur after 3h. shaking time, after this period when leaving the phases in contact with shaking for more than 24h. the amount of desorbed $Pb^{2+}$decreased to 60%.45%,15% on sugarcane sample using $10^{-1}$M, $10^{-2}$M and $10^{-3}$M $MnCl_2$ respectively, as shown in Fig.(12) which means that the some amounts of $Pb^{2+}$ are readsorbed again on sugarcane sample. The same behavior occurs also for rice, wheat and maize straw as shown in Figs.(13-15).

Desorption study of Pb(II) using distilled water and $10^{-1}$M of EDTA as eluents have been tested. It is observed that no desorption is achieved in this case. i.e. $H_2O$ is not suitable as leaching agent forPb(II) adsorbed on the straw used. This finding may mean that $H_2O$ as an

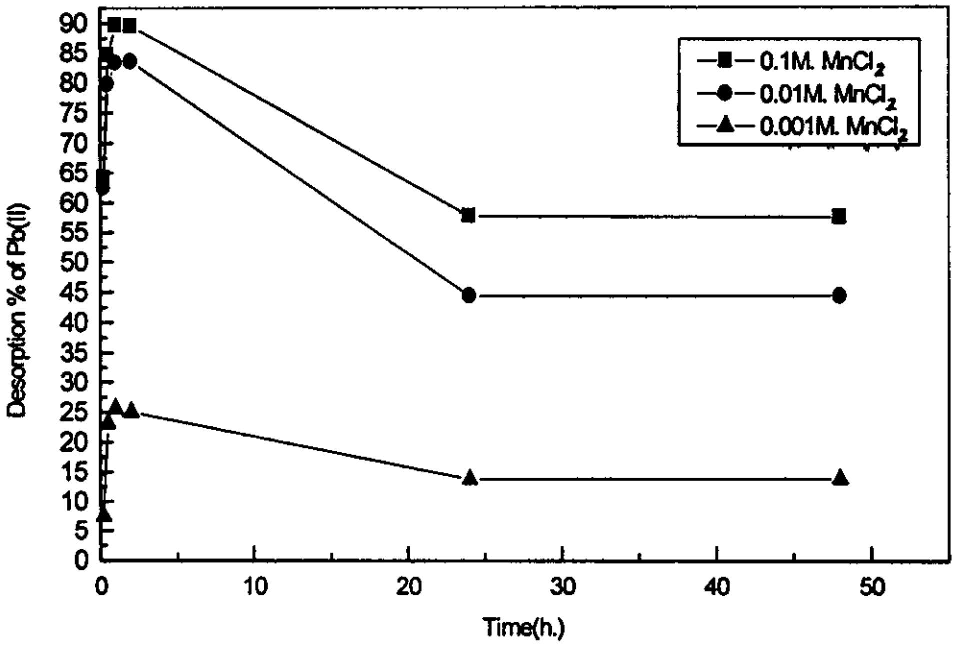

Fig.(12)Effect of contact time on desorption of Pb(II) from sugarcane residue sample using $MnCl_2$ solutions.

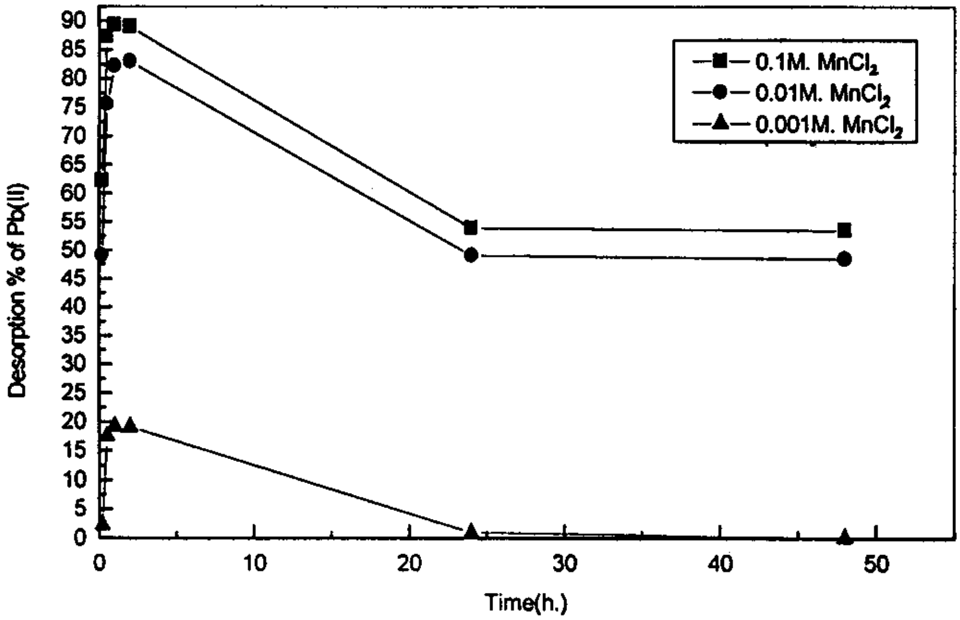

Fig.(13)Effect of contact time on desorption of Pb(II) from rice straw sample using $MnCl_2$ solutions.

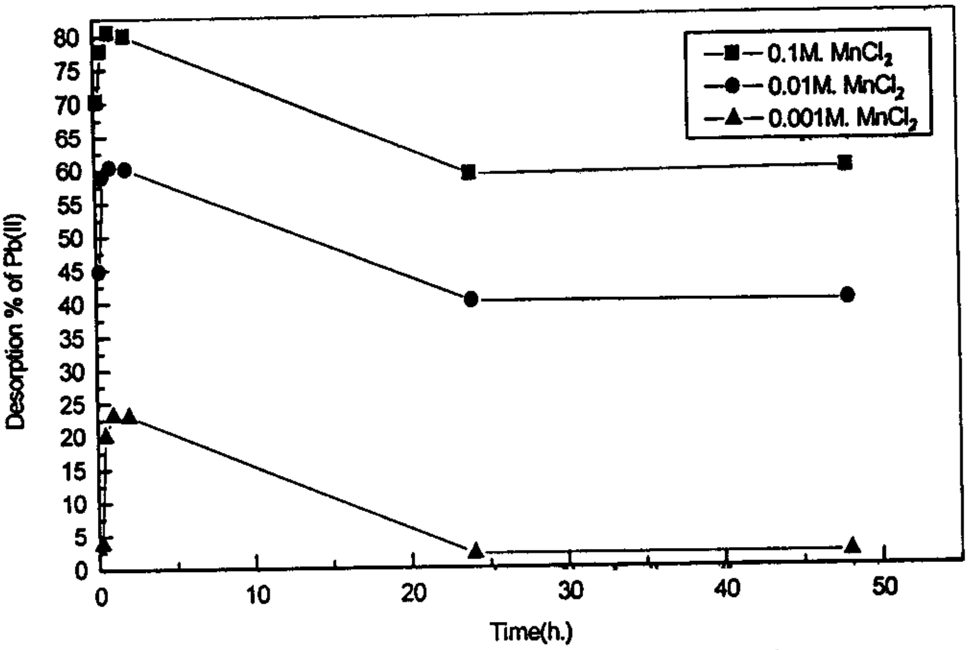

Fig.(14)Effect of contact time on desorption of Pb(II) from maize straw sample using MnCl$_2$ solutions.

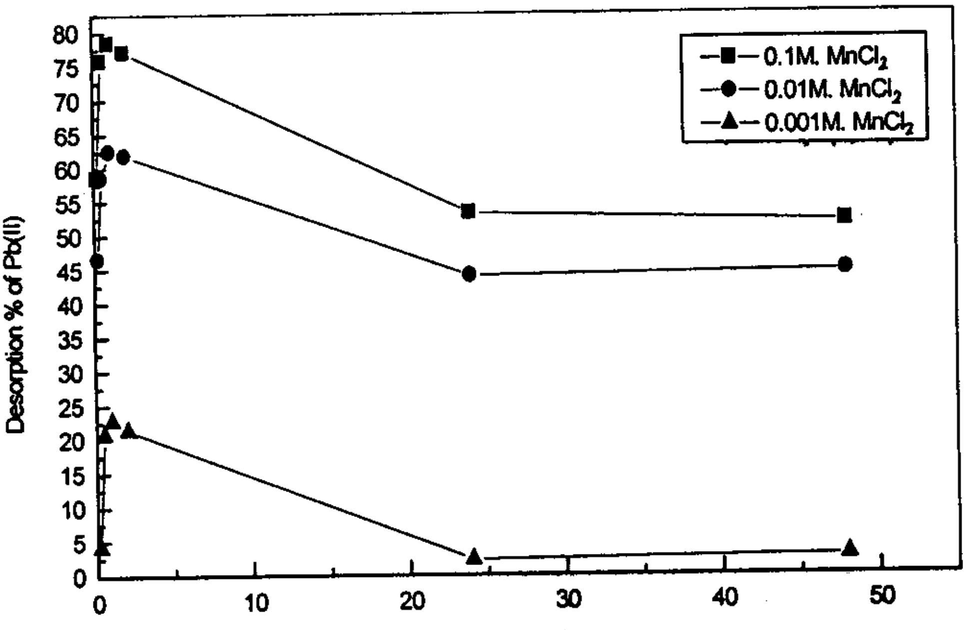

Fig.(15)Effect of contact time on desorption of Pb(II) from wheat straw sample using MnCl$_2$ solutions.

eluent hardly attacks the interaction taking place between the metal ion and the sorbent surface(139).

### 3.4.6. Adsorption-Desorption Recycling studies of Pb(II)

Table (11) shows the results of recycling steps of adsorption-desorption studies of Pb(II) using a nitrate solution of pH=5 and $10^{-1}$M of $MnCl_2$ solution. Uptake % of Pb(II) reached 97.9% on rice straw (first use of rice straw sample). Then the desorption of Pb(II) from rice straw sample using $10^{-1}$M $MnCl_2$ reached 86.6% in the first desorption cycle. In the second desorption cycle, by successive desorption experiment, the desorption of Pb(II) reaches 99.4%. After the last desorption cycle the rice straw was reused for a new adsorption process of Pb(II) from nitrate media of pH=5. The adsorption of Pb(II) on this reused sample reached 95.8%. Shaking time for each experiment was one hour. The same trend of recycling interpretation was achieved for the other straw and the sugarcane residue used. From these results it is clear that all the straw and the sugarcane residue samples could be reused successfully for adsorption of Pb(II) with a very high uptake percentage. Also, these samples could be cleaned almost completely from the adsorbed Pb(II) by only two successive desorption experiments.

This achievement recommends the use of regenerated straw by several recycling steps in a semipilot work for cleaning the environment from Pb(II) by a certain designed model for this purpose. As a simple application for this idea, Fig.(16) shows the percentages of Pb(II) sorbed on rice straw sample during four successive experiments of adsorption and desorption steps.

Table(11) Uptake and Desorption percentages of Pb(II) on different straw and sugarcane residue samples using nitrate media of pH = 5 and $10^{-1}$ M. $MnCl_2$ in recycling steps one hour shaking time each

| Samples | Uptake % of Pb(II).(1st use of samples) | Desorption % of Pb(II) (1st cycle) | Desorption % of Pb(II) (2nd cycle) | Uptake % of Pb(II).(2nd use of samples) |
|---|---|---|---|---|
| Sugarcane | 98.3 | 88.66 | 96.1 | 96.0 |
| Rice Straw | 97.9 | 86.6 | 99.4 | 95.8 |
| Maize Straw | 97.2 | 79.4 | 100 | 94.3 |
| Wheat Straw | 96.9 | 74.9 | 99.9 | 91.6 |

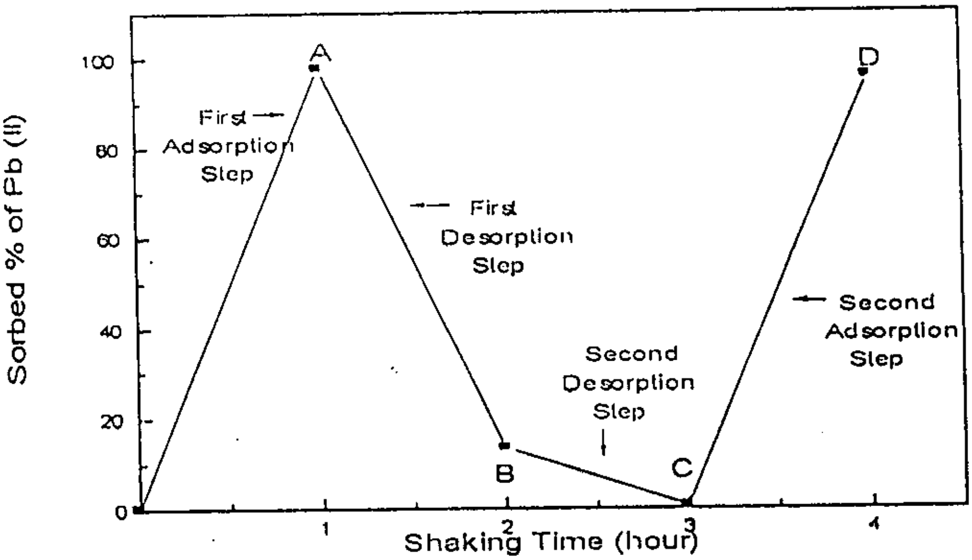

Fig.(16) A complete cycle for use and reuse of rice straw as a test for semipilot application

Figure (16) is considered to be a proposal for decontaminating environmentally lead polluted wastes on a semipilot scale. This process could be achieved through four hours steps. At point (A), 97.9% of Pb(II) could be adsorbed on R.S sample after one hour shaking time at pH=5. At point (B), 13.4% of Pb(II) is found to be remained on R.S sample after another one hour shaking time using $10^{-1}$M $MnCl_2$ solution. At point (C), 0.6% of Pb(II) is found to be remained on R.S sample after another one hour shaking time using $10^{-1}$M $MnCl_2$ solution. At point (D), the obtained R.S sample is reused for adsorption of new Pb(II) from a newly added solution of pH=5. Obviously the whole process proceeds through approximately four hours.

## Studies on Radioactive Isotopes:

### 3.5. Adsorption/ Desorption studies of Co(II):

In these studies the radioisotope $^{60}Co$ was used and its amount was assayed radiometrically as described in the former chapter.

### 3.5.1. Effect of pH:

The uptake of Co(II) was studied from sulfate solution on the three types of straw and the sugarcane samples, Fig.(17). From this figure it is indicated that the highest uptake of Co(II) from the sulfate solution of pH=3.5 on R.S, S.C, M.S and W.S is 57.5%, 50%, 41.7% and 23.9% respectively. Further increase of pH above 3.5 gives rise to a decrease in the uptake. The high adsorption of $Co^{2+}$ may be attributed to the small ionic radius of $Co^{2+}$ (0.76A°). Thus, Co(II) should penetrate more deeply into the lattice structure of adsorbent surface where it is irreversibly fixed(140,141).

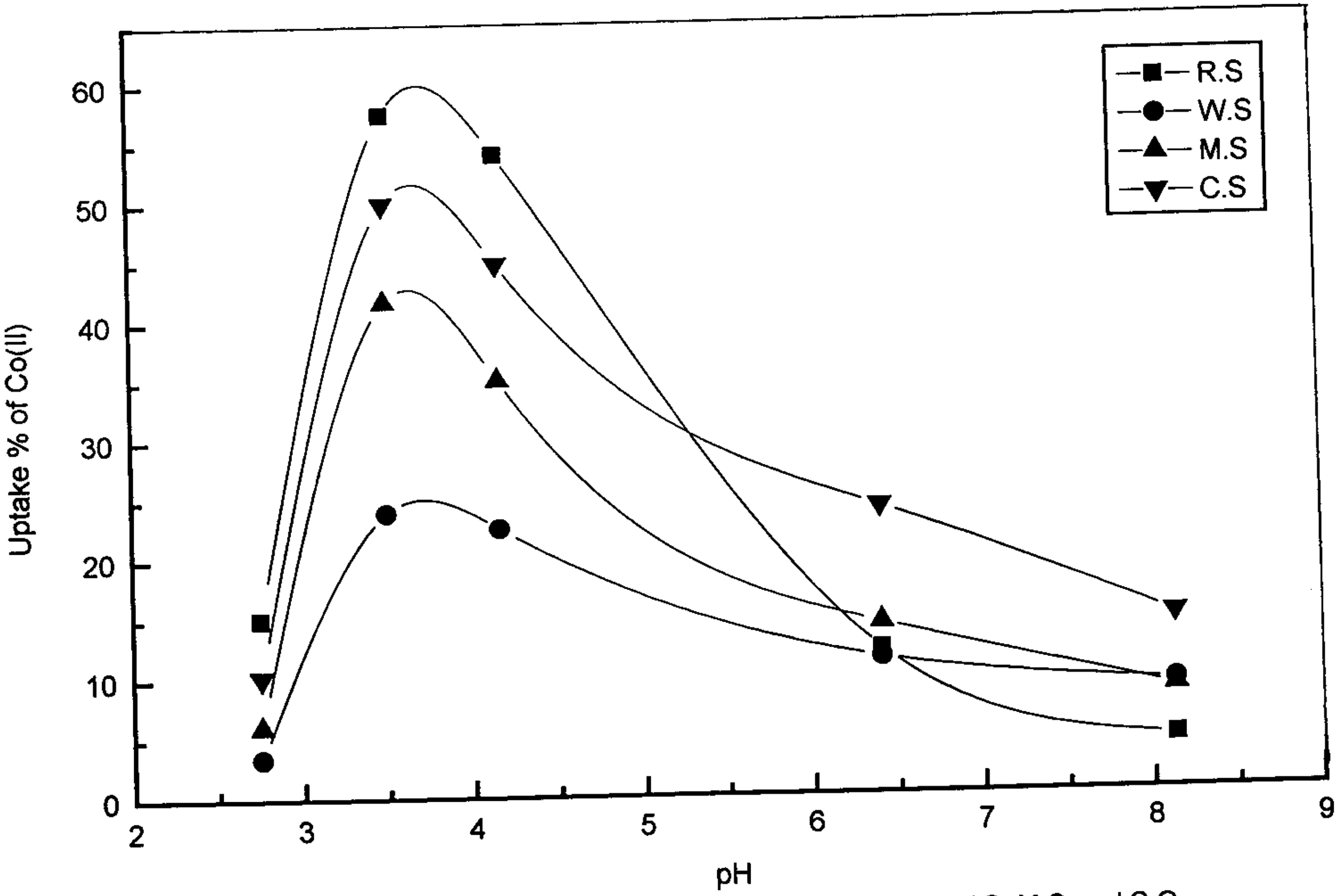

Fig.(17) Effect of pH on adsorption of Co(II) on R.S, W.S, M.S and S.C

### 3.5.2. Effect of contact time:

The effect of contact time on the sorption of Co(II) on R.S& W.S& M.S and S.C samples from sulfate solution at pH=3.5 is given in Fig.(18). This figure represents the relation between the shaking equilibration time and the uptake percent of Co(II). The curves show that the highest uptake % of Co(II) on R.S& W.S& M.S and S.C is 55%, 25%, 38% and 49% respectively after 3h. shaking. So, the equilibrium time accepted in this system is 3h., for which, it is used in the following studies.

### 3.5.3. Effect of carrier concentration:

The adsorption isotherm of Co(II) on different straw samples studied was done by using different concentrations of $CoCl_2$. The amount of Co(II) adsorbed per gram (X/m) in meq.$g^{-1}$ on wheat straw and sugarcane samples is plotted against Co(II) concentration [C] on logarithmic scale as shown in Fig.(19). The plots in this figure give straight line of slope=1. This linearity of the isotherm means that the adsorption process follows Freundlich isotherm. In agreement with other authors(118) this means that the adsorption of Co(II) on the sorbents used takes place through the formation of a single monolayer of the sorbed ionic species. These results are in a good agreement with that published for the adsorption of various metal ions on cellulose(119), and wood powder(80,120). Hence the uptake of Co(II) on maize straw follows the same mechanism for the adsorption of similar metal ions on cellulose and the wood powder.

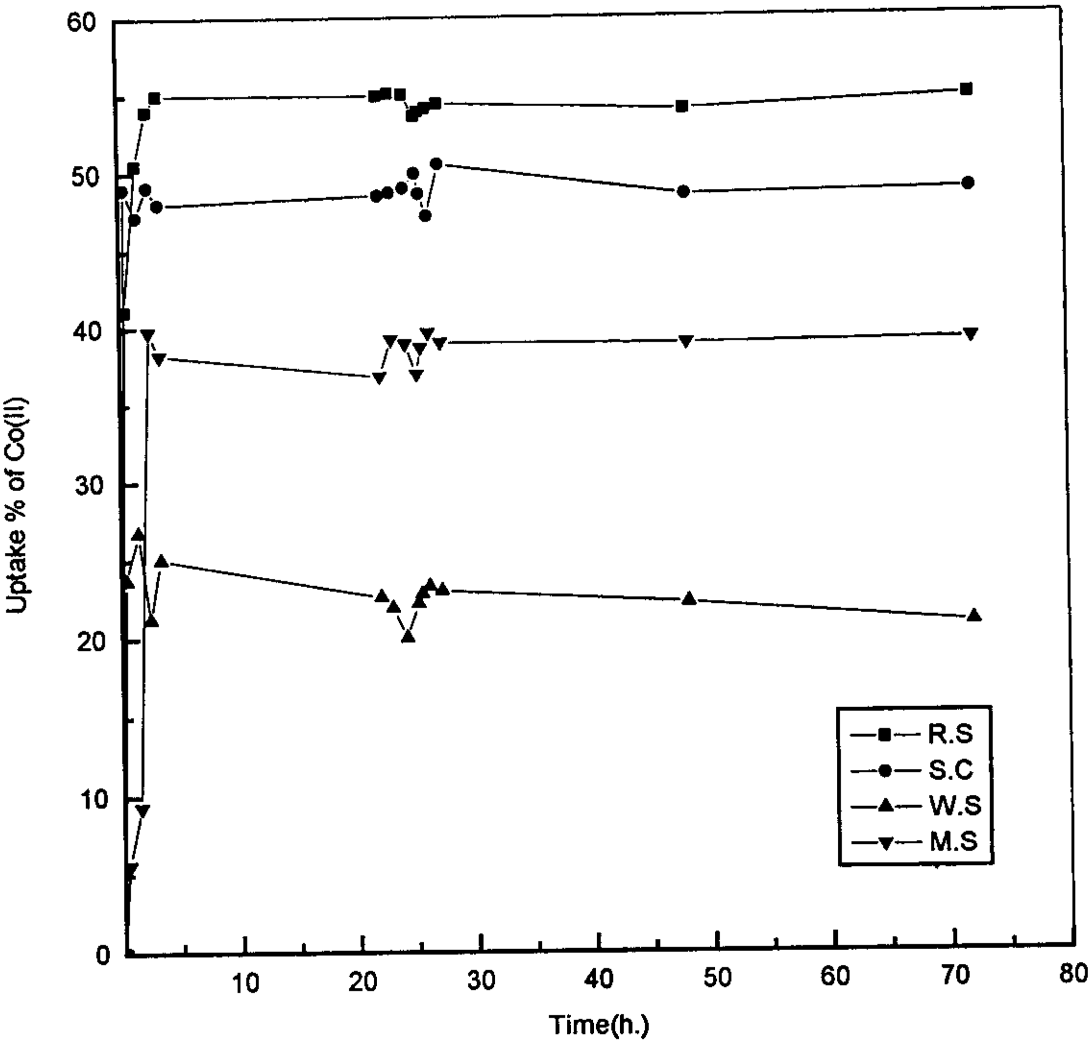

Fig.(18) Effect of contact time on adsorption of Co(II) on R.S, W.S, M.S and S.C samples from sulfate solution at pH=3.5

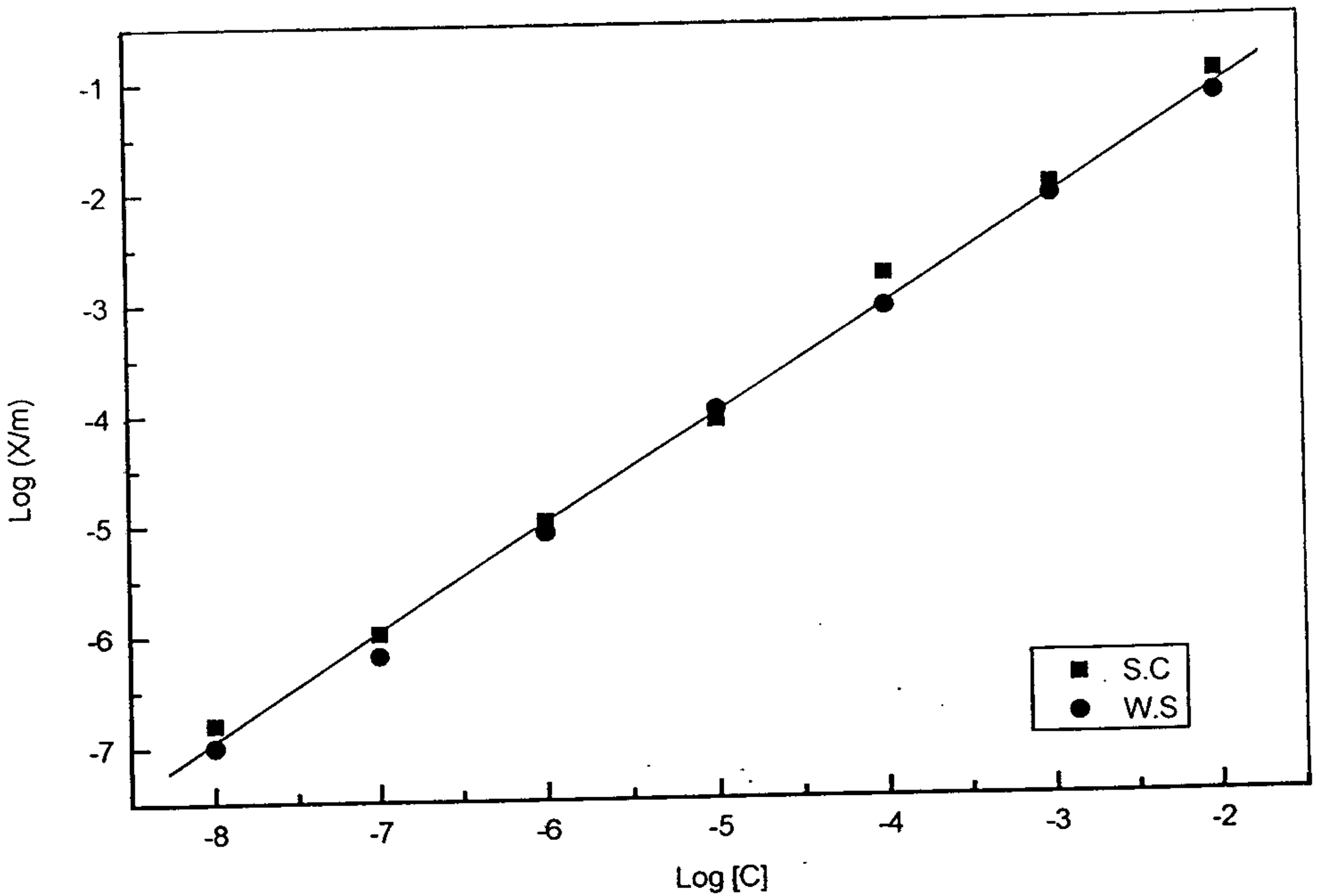

Fig.(19) Effect of carrier concentration on the adsorption of Co(II) on W.S and S.C samples.

### 3.5.4. Desorption studies of Co(II):

In this case the effect of contact time on desorption of Co(II) from maize straw and sugarcane residue samples using either distilled water or solutions containing different concentrations of a similar cation ($Mn^{2+}$). Desorption of Co(II) from maize straw and sugarcane residue samples by $H_2O$ as eluent reaches ~ 9%, Fig.(20). On the other hand, solutions with different concentrations of $MnCl_2$ were used as eluents for washing Co(II) cations from straw and sugarcane samples, Figs.(21- 23). Washing the Co(II) loaded sugarcane samples with solutions of $10^{-1}$M $MnCl_2$ gives a desorption of 27%. This value decreases with the decrease of $MnCl_2$ concentration. The data of such experiments shows that the percent of Co(II) eluted by $H_2O$ is lower than its corresponding value which was eluted by different concentrations of $MnCl_2$; where the $Mn^{2+}$ cation is similar in charge and ionic radius to the loaded Co(II) cation (where ionic radius of $Co^{2+}$= 0.76 $A^{\circ}$ and for $Mn^{2+}$=0.8 $A^{\circ}$) on the sugarcane samples. So, the elution of the loaded Co (II) through the replacement of similar cations may be enhanced to a certain degree. Hence, the finding obtained in this study shows that sugarcane residue can be used in the separation processes of different cations taking place in nuclear technology processes.

### 3.6. Studies on Eu(III):

### 3.6.1. Effect of pH on the sorption of Eu(III):

Data of the effect of pH variation on the sorption of Eu(III) on sugarcane residue and straw samples from sulfate solutions is given in Fig. (24). The plots in this figure show that the highest uptake % of

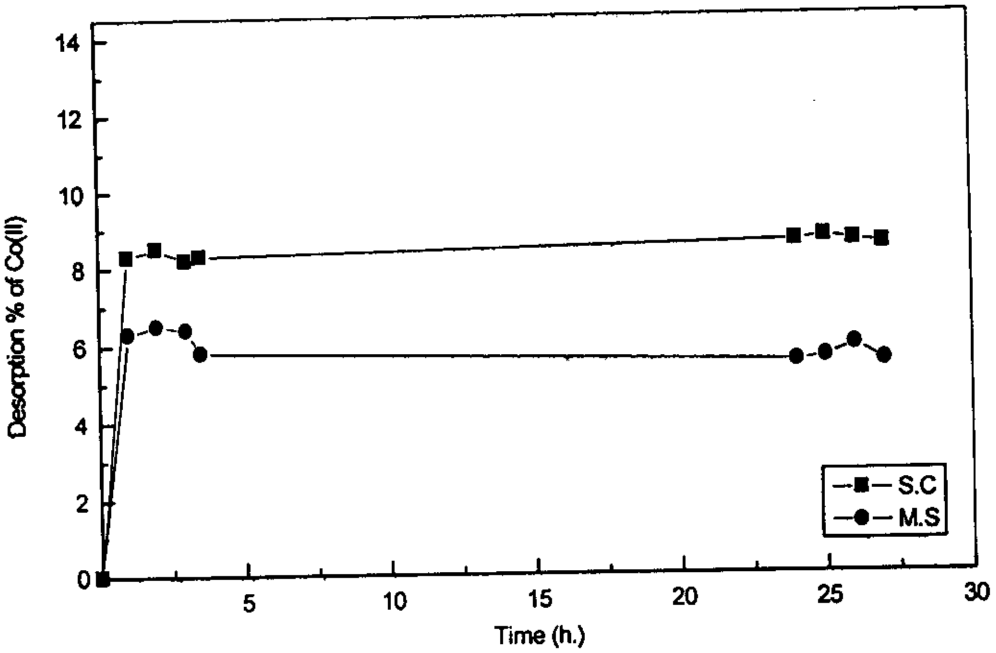

Fig.(20) Effect of contact time on desorption of Co(II) from sugarcane (S.C) and maize straw (M.S) samples using $H_2O$.

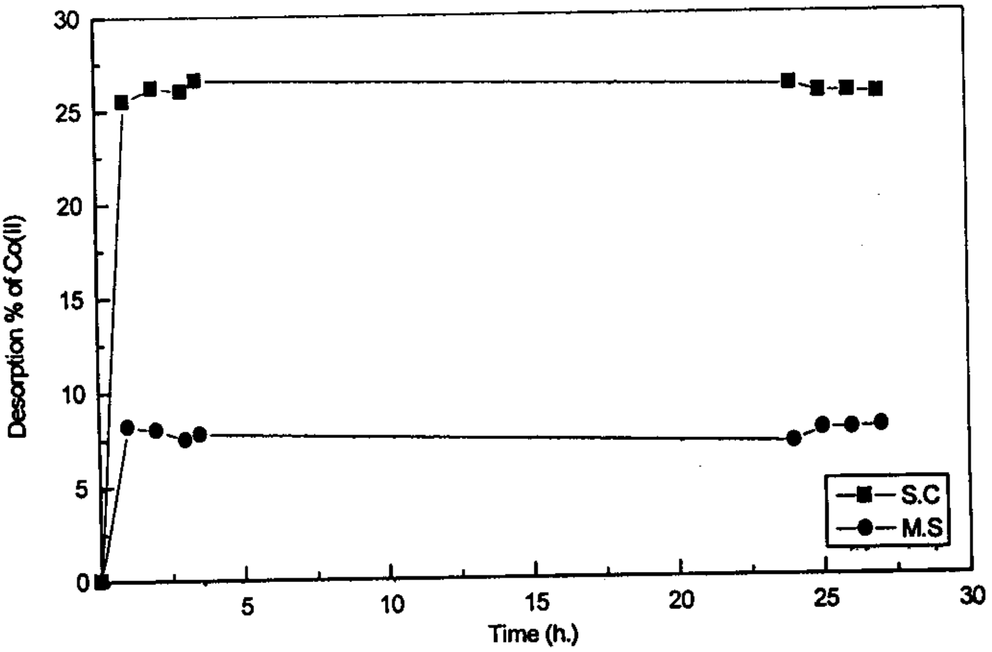

Fig.(21) Effect of contact time on desorption of Co(II) from sugarcane (S.C) and maize straw (M.S) samples using 0.1M $MnCl_2$.

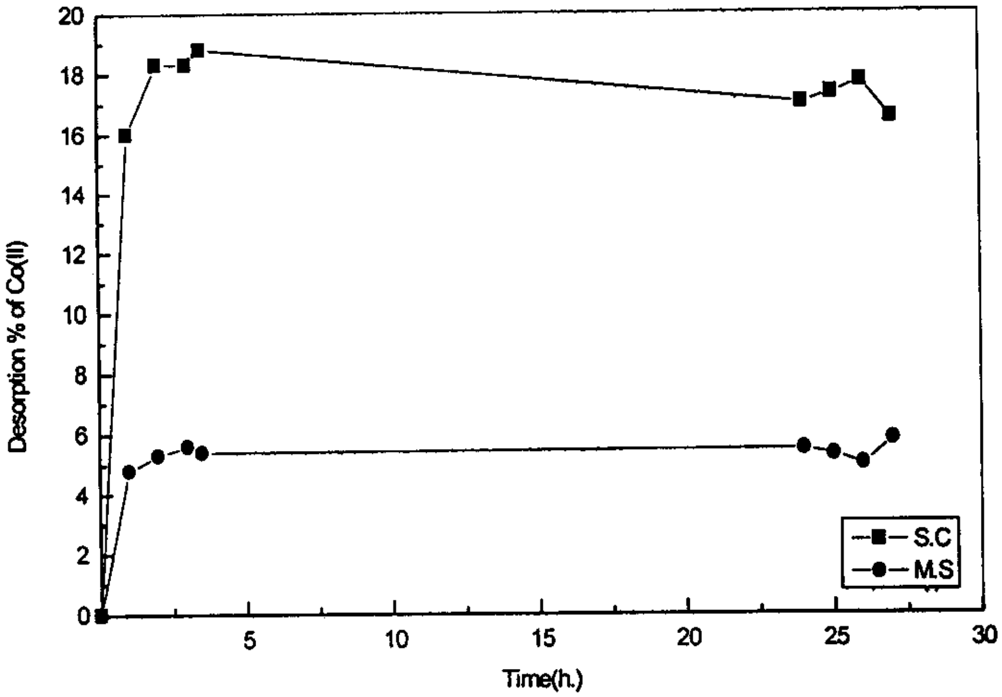

Fig.(22) Effect of contact time on desorption of Co(II) from sugarcane (S.C) and maize straw (M.S) samples using 0.01M $MnCl_2$

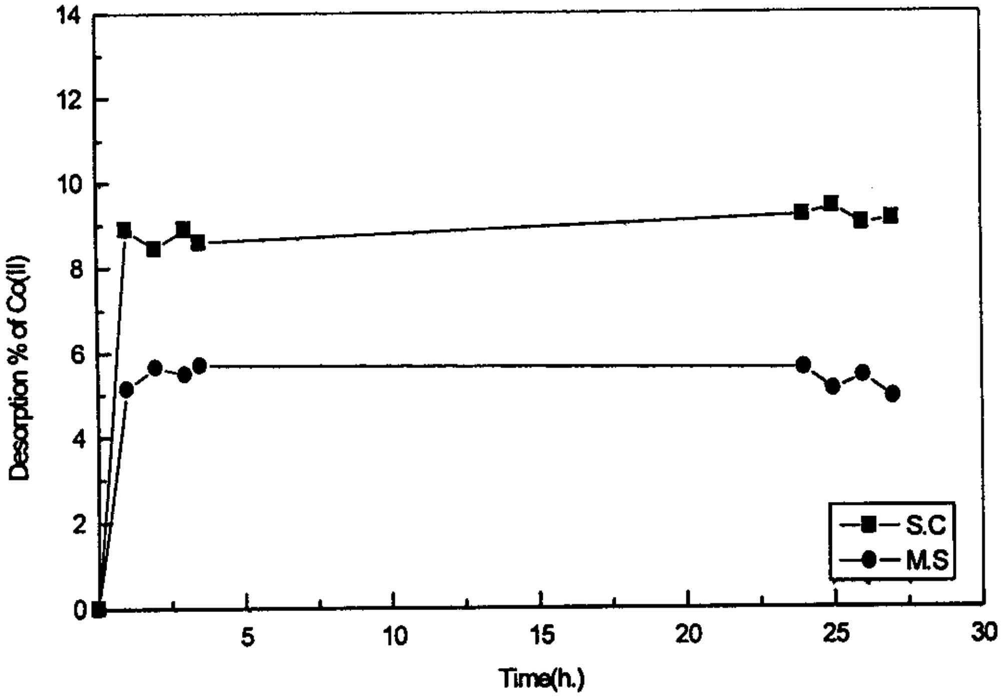

Fig.(23) Effect of contact time on desorption of Co(II) from sugarcane (S.C) and maize straw (M.S) samples using 0.001M $MnCl_2$

Eu(III) on straw samples reaches 80% at pH=3.5 and that for sugarcane, it reaches 78% at pH=3. The decrease in Eu(III) sorption with increasing pH value above the $pH_{max.}$ may be ascribed to the hydrolysis of Eu(III) ions forming polyhydorlytic products as reported by Moller(142). Depending on this trend, similar studies were carried(143) out using treated fly ash.

### 3.6.2. Effect of HCl and Oxalic acid on the sorption of Eu(III):

The effect of the variation of both HCl and oxalic acid concentrations on the sorption of Eu(III) on sugarcane residue and the different straw samples are presented in Figs.(25) and (26) respectively. It is clear that no clear difference occurs for the sorption behavior of Eu(III) in the two cases. Where, sorption of Eu(III) on sugarcane residue decreases to the lowest value of 5.36% at acid concentration of 1N HCl. Also, decreases to the lowest value of 5.3 at acid concentration of 1N oxalic acid. Then, Eu(III) sorption increases gradually till it reaches its highest values of 62.9% at 3N HCl and 70% at 3N oxalic acid. Under the experimental conditions studied it is also obvious that the nature of the anion ($Cl^-$ or oxalate) in the aqueous phase has little or perhaps no influence on the sorption of Eu(III) on the sorbents used.

### 3.6.3. Effect of contact time:

The effect of contact time on the adsorption of Eu(III) from nitrate media of pH=3.5 on the studied sorbents are given in Fig.(27a) (dynamic adsorption). It is obvious that Eu(III) (sorption) uptake % reaches its maximum value for straw samples 75% after a shaking time of 80min. and at the same time it reaches its equilibrium state. The same figure also

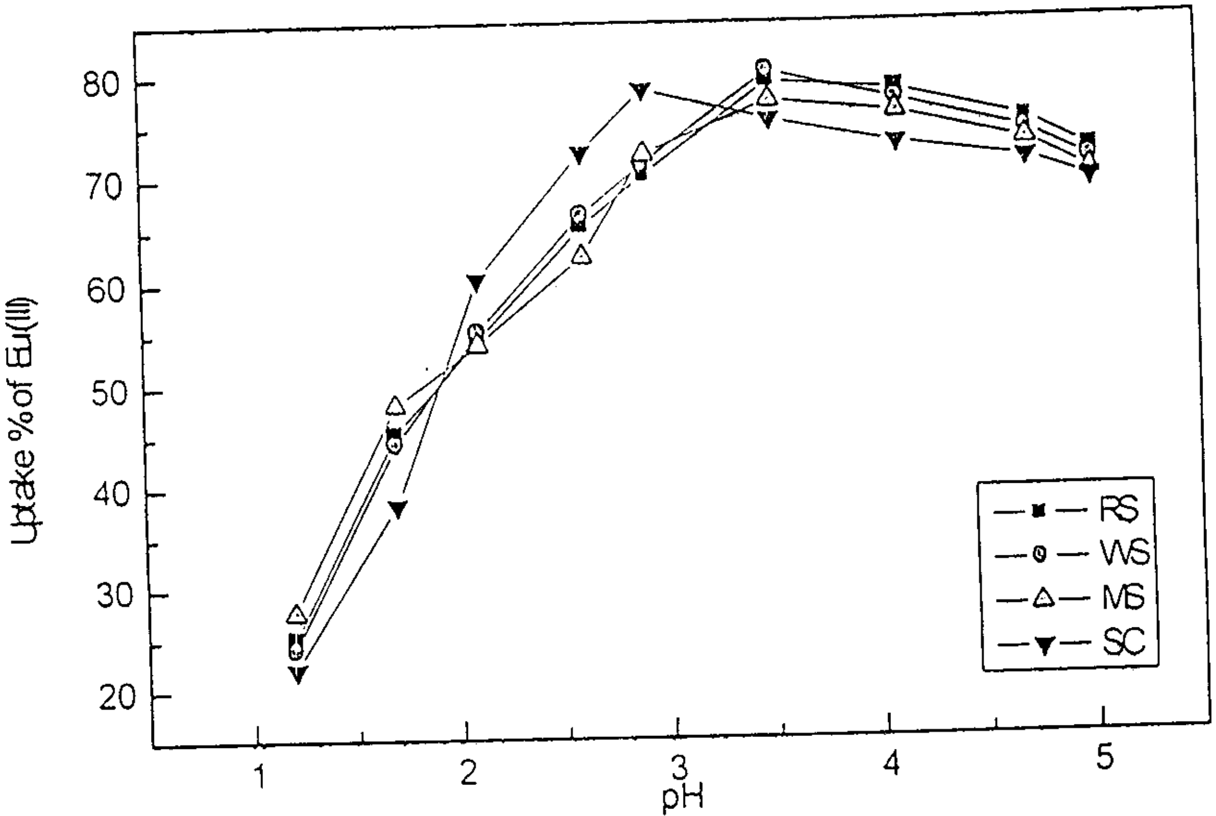

Fig.(24) Effect of pH variation on adsorption of Eu(II) on different straw and sugarcane samples from sulphate solution.

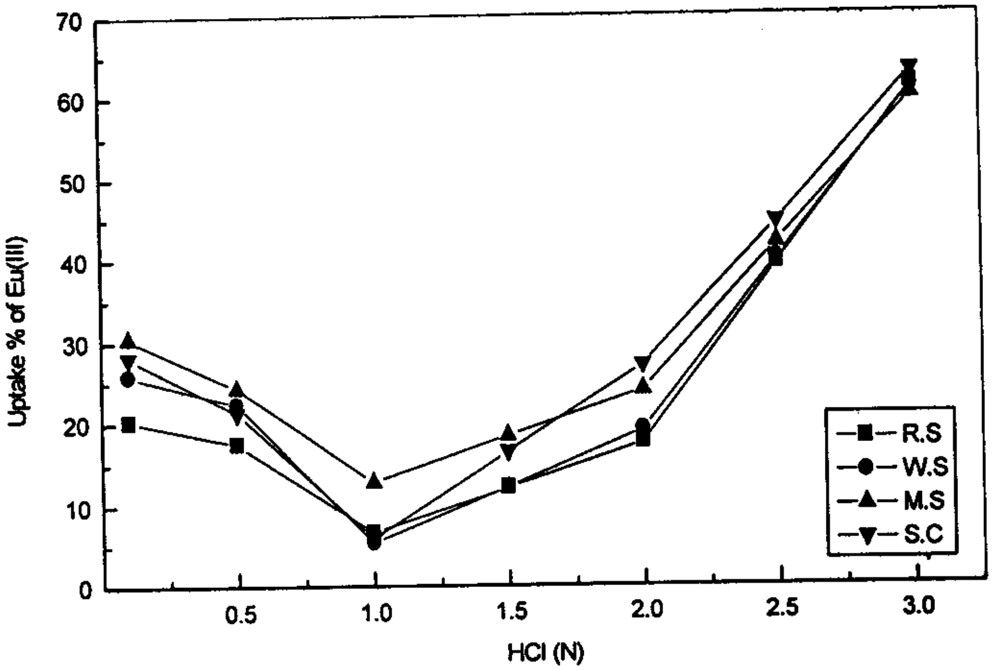

Fig.(25)Effect of hydrochloric acid concentration on adsorption of Eu(III) using different straw and sugarcane samples.

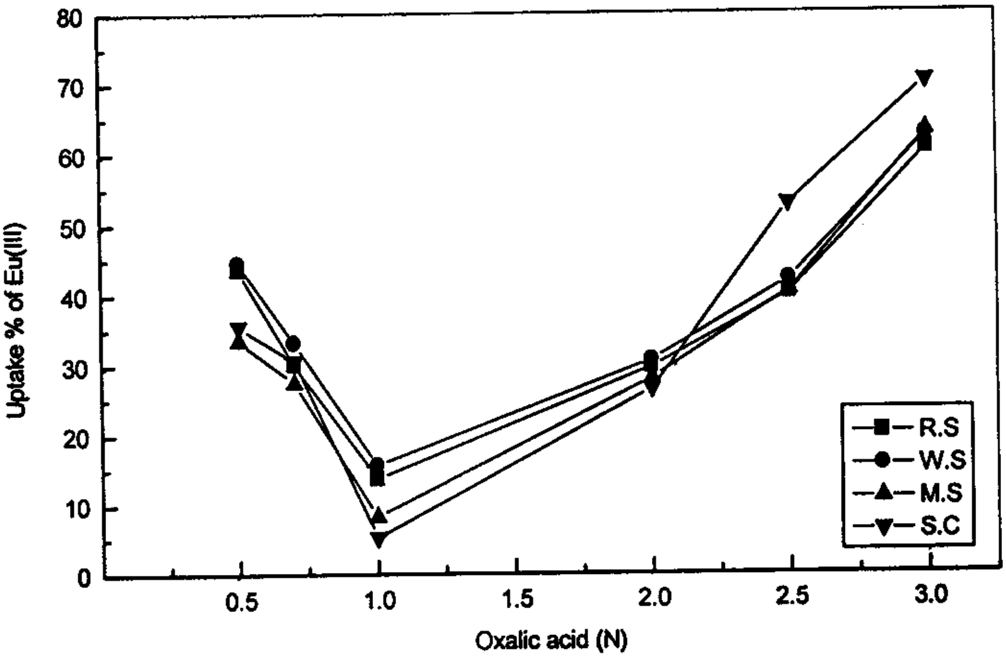

Fig.(26)Effect of oxalic acid concentration on adsorption of Eu(III) using different straw and sugarcane samples.

shows that the amount of Eu(III) sorption on the straw and sugarcane samples used are quiet similar.

The sorption of Eu(III) from nitrate solution of pH=3.5 was studied statically on rice straw and sugarcane samples, Fig.(27b). The uptake % of Eu(III) reaches 80% on sugarcane sample and 75% on different straw samples at 16h. these uptake percentages are nearly the same, which are obtained in the former dynamic sorption case but the equilibrium time is 80min. So, it could be deduced that 2h. contact time is enough for shaking the two phases when studying the effect of other parameters on the sorption process. From the values of uptake % of Eu(III), it is indicated that no difference between the three types of straw in addition to sugarcane residue samples used.

Effect of contact time on the sorption of Eu(III) on rice straw sample from distilled water of pH=5.2 has been investigated, Fig.(28). Eu(III) uptake % reaches its maximum values 65% and 60% for sugarcane and rice straw samples respectively after shaking time = 80min. These values are lower than those obtained from nitrate solution. Such behavior makes the use of these naturally cheap materials for sorping Eu(III) from distilled water of pH=5.2 without using any chemicals is advantageous. It is observed that uptake of Eu(III) on sugarcane from the studied media is slightly higher than the other straw samples.

### 3.6.4. Effect of carrier concentration:

The effect of carrier concentration on the sorption percentage of Eu(III) is shown in Fig.(29). Different concentrations of stable europium

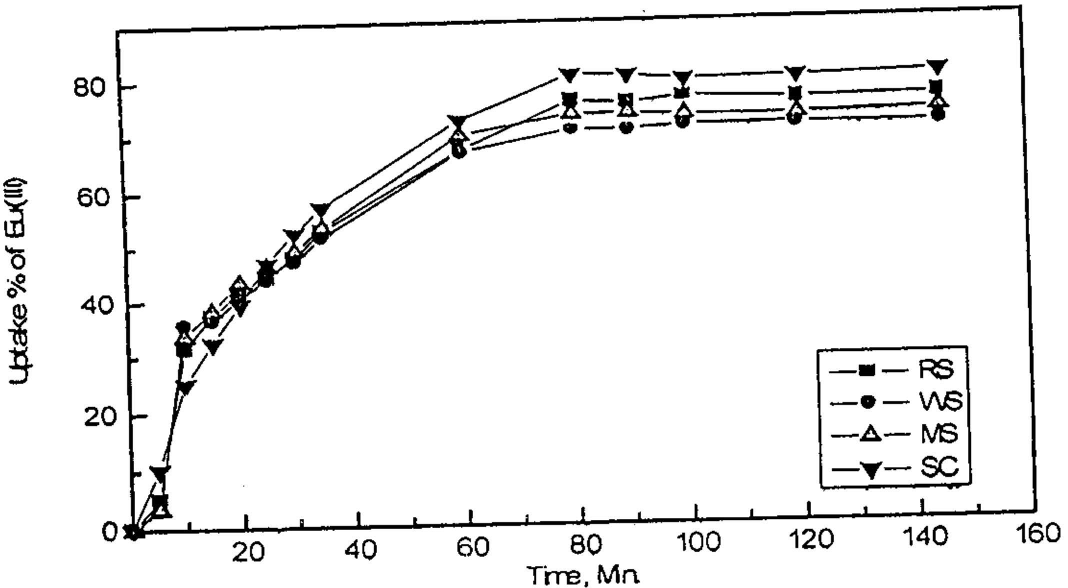

Fig.(27a) Effect of contact time on the adsorption of Eu(III) on different straw and sugarcane samples from nitrate media of pH=3.5

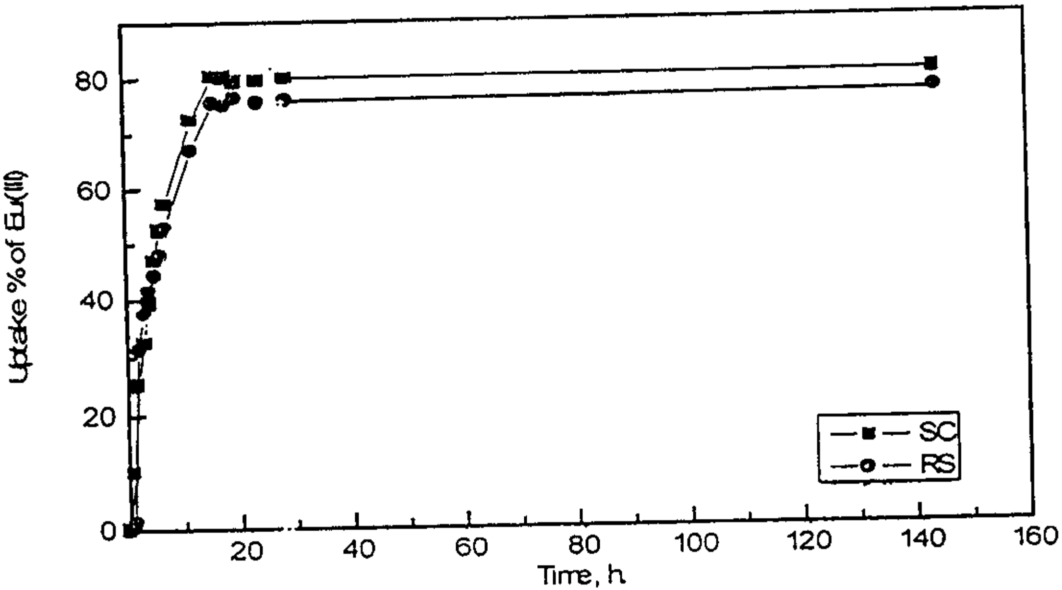

Fig.(27b) Effect of contact time on the adsorption of Eu(III) on rice straw and sugarcane samples from nitrate media of pH=3.5 (Staticaly)

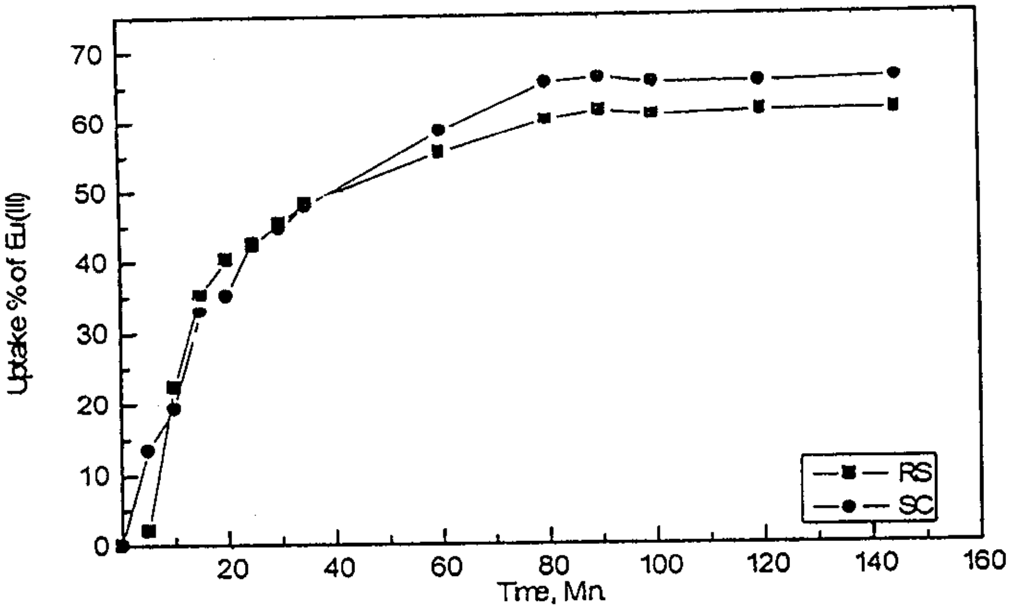

Fig.(28) Effect of contact time on the adsorption of Eu(III) on rice straw and sugarcane samples from distiled water of pH=5.2

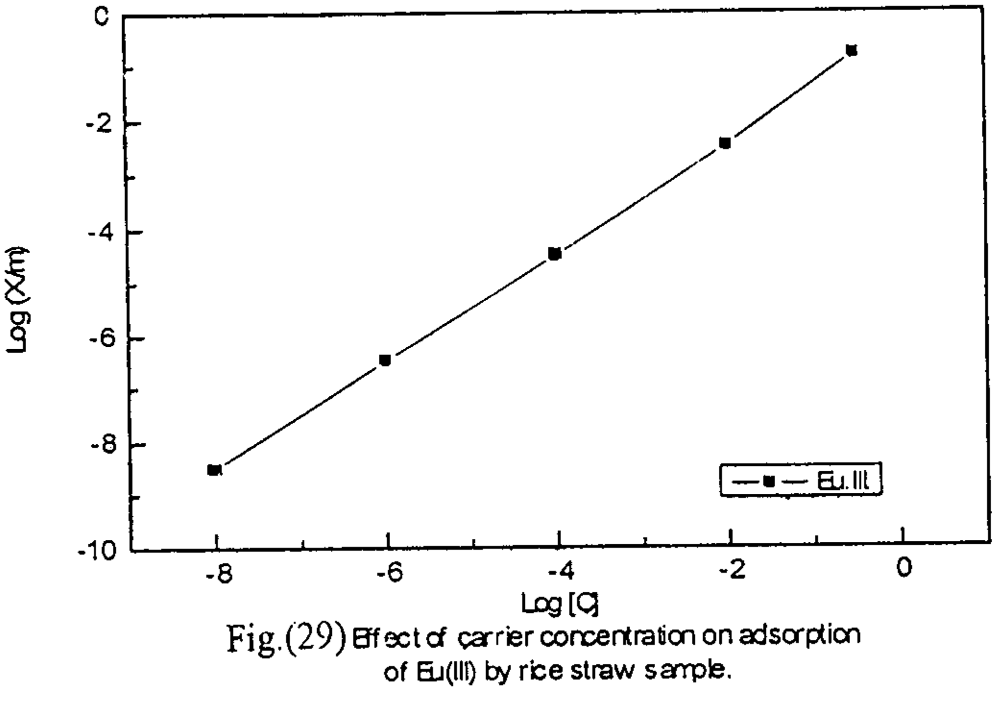

Fig.(29) Effect of carrier concentration on adsorption of Eu(III) by rice straw sample.

nitrate, $Eu(NO_3)_3$ are added to active europium and the sorption of Eu(III) from the nitrate solution of pH=3.5 on rice straw sample has been investigated. The amount of Eu(III) sorbed per gram (X/m) in meq.$g^{-1}$ is plotted against the carrier concentration [C] on a logarithmic scale. The relation obtained is linear with slope = 1 and the amount of Eu(III) sorbed per gram increases as the carrier concentration is increased. This finding follows the Freundlich isotherm.

### 3.7. Studies on Cs(I):

### 3.7.1. Effect of pH:

The effect of pH variation on the sorption of Cs(I) on different straw and sugarcane residue samples has been investigated, Fig.(30). The maximum uptake % of Cs(I) by rice straw and sugarcane samples are 49.6% and 38% respectively, and occurs at pH=7.1, followed by a decrease with increasing the pH. This observation could be accounted for by the change that may occur on the surface charge of the adsorbent by changing the pH. Worth mentioning here that, at low pH (increase in the hydrogen ion concentration), there is a competation between $Cs^+$ and $H^+$ for sorption on the sorbent surface leading to a decrease in Cs(I) uptake (adsorption) and vice versa when increasing the pH (i.e. decreasing the hydrogen ion concentration). The maximum adsorption of radiocesium occurs in neutral medium (pH=7.1) since the $Cs^+$ cations have a large ionic radius (1.69A°)(140). This means that a large ionic radius show the ability to compress the electric double layer which is present around the adsorbent particles ($H^+$ ions) and reduce the electrokinetic potential(144). Voyutsky(145) gave a detailed explanation of the decrease and increase in Cs(I) uptake with varying the pH.

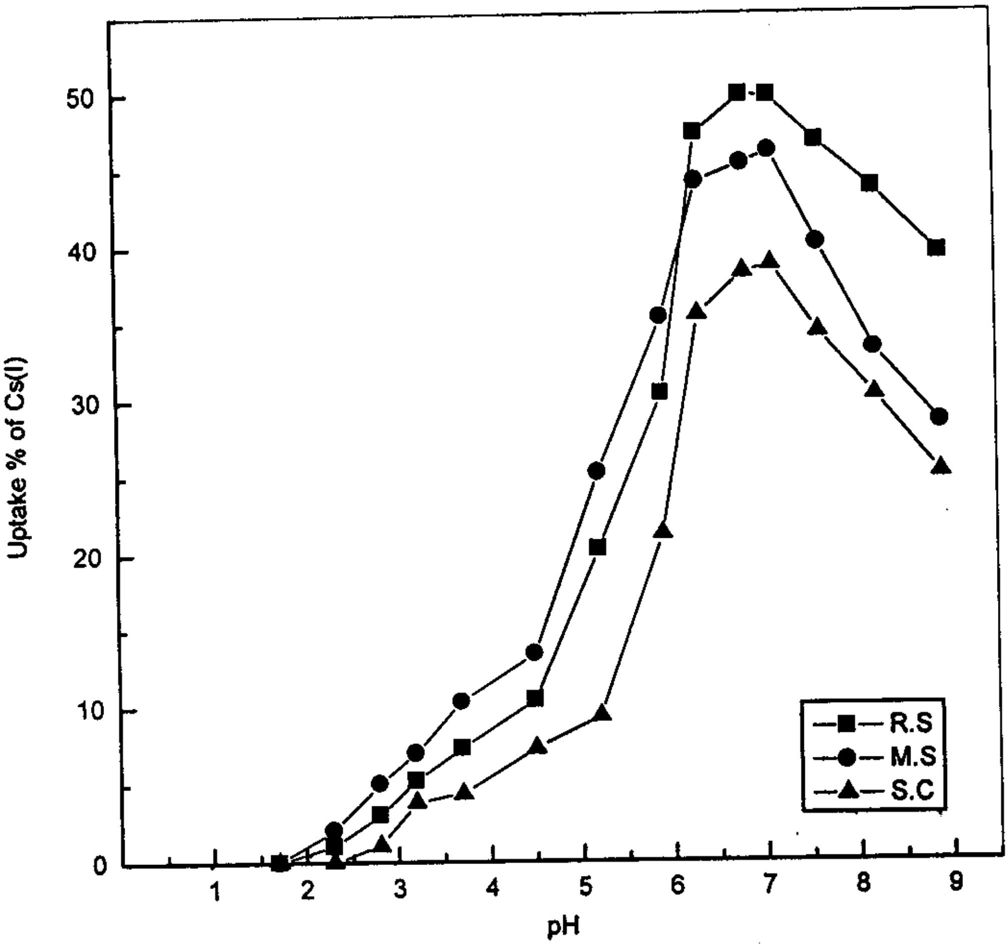

Fig.(30) Effect of pH variation on adsorption of Cs(I) on different straw and sugarcane samples.

### 3.7.2. Effect of contact time:

The sorption of Cs(I) on different straw and sugarcane samples from ammonia solution of pH=7.0 was represented against the contact time in Fig.(31). With sugarcane the uptake % reaches 40% after 2h. of shaking time. For straw samples the uptake % reaches 50% after 75min. of shaking time at which the equilibrium is attained for straw samples. The effect of contact time on the sorption of Cs(I) on rice straw and sugarcane samples from distilled water of pH=5.2 has been investigated and results are given in Fig.(32). The plots in this figure show unexpected Cs(I) uptake = 80% in a short time after 10min. shaking time. Then Cs(I) uptake decreases sharply to get equilibrium after 80min. reaching 20% and 10% for rice straw and sugarcane samples respectively.

For different straw and sugarcane samples, data in Figs. (3a, 3b, 9, 18, 27a, and 31) in this chapter shows that the sequence of sorption capacity is trivalent > divalent > monovalent cations. This sequence of sorption on the straw and sugarcane samples agrees with the sequence of chemisorption of the cations which is explained on the bases of the tendency of such cations to form complexes within the adsorbent and this result agrees with Belacy et al.(146). The low uptake of $Cs^+$ ion compared with the other ions could be due to its large ionic radius (1.69A°) relative to $Co^{2+}$ (0.76A°), $Pb^{2+}$ (1.37A°), $Cr^{6+}$ (0.69A°) and $Eu^{3+}$ (1.12A°). The large ionic size of Cs(I) causes a lower diffusion and hence a smaller penetration of Cs(I) into the micropores of the adsorbent surface.

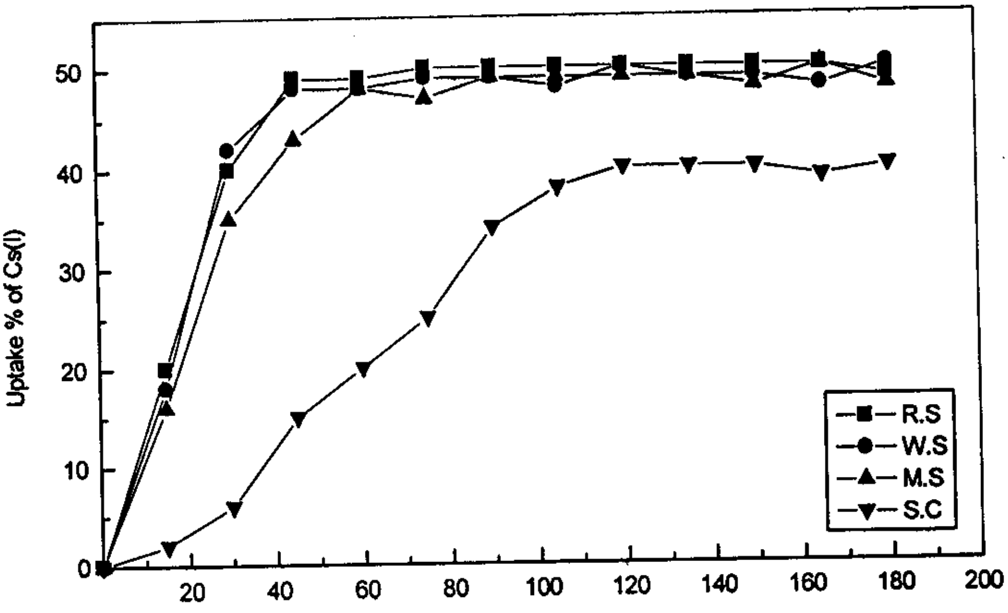

Fig.(31) Effect of contact time on adsorption of Cs(I) from ammonia solution at pH=7 using different straw and sugarcane samples.

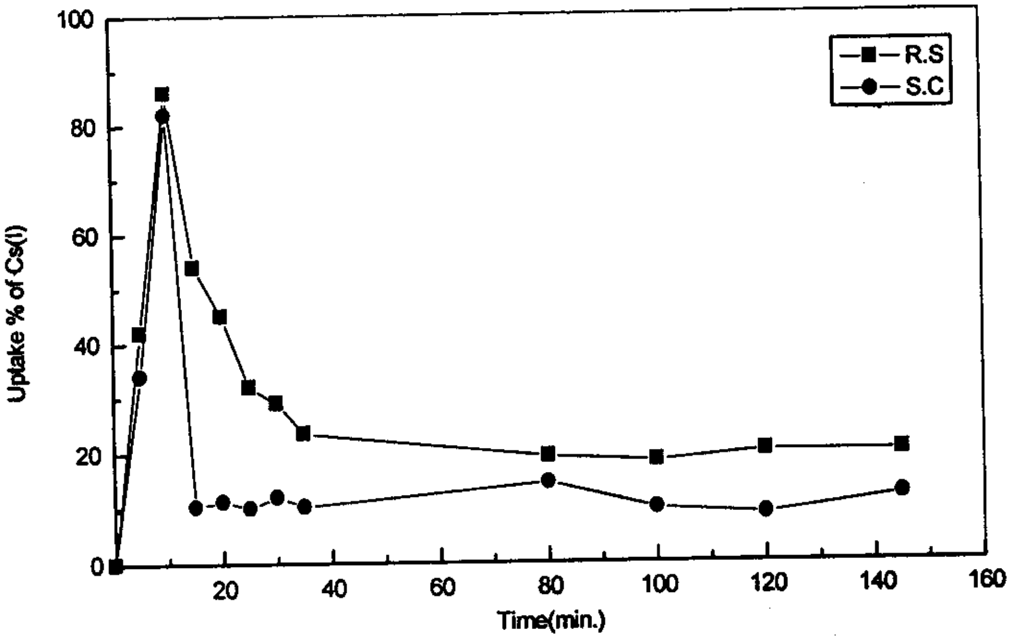

Fig.(32) Effect of contact time on adsorption of Cs(I) on rice straw and sugarcane samples from distilled water of pH=5.2

### 3.7.3. Effect of carrier concentration:

Different concentrations of CsCl were added to active cesium to study the sorption of Cs(I) from ammonium solution of pH=7.0 on rice straw sample has been investigated in Fig.(33). The amount of Cs(I) sorbed per gram (X/m) in meq.g$^{-1}$ was plotted against the carrier concentration [C] on logarithmic scale. The plot gives a straight line of slope nearly 1 and this linearity means the formation of a single monolayer from the adsorbed Cs(I) cations on different straw and sugarcane samples and this agree with Freundlich isotherm.

### 3.7.4. Desorption of Cesium:

The desorption of Cs(I) from different straw and sugarcane residue samples was studied using both distilled water and solutions of different concentrations of NaCl ($10^{-1}$M& $10^{-2}$M and $10^{-3}$M). Desorption of Cs(I) by $H_2O$ as eluent was shown in Fig.(34). The plot in this figure indicated that 65% of Cs(I) was eluted after 30 minutes shaking time. After this period, when leaving the phases in contact with shaking for more than 24h. the amount of Cs(I) desorbed decreased to 45% on S.C sample. This mean that 20% of the amount of eluted cesium is readsorbed again on S.C and this behavior occurs also for rice, wheat and maize straw samples. On the other hand, the desorption of Cs(I) from different straw and sugarcane residue samples using different concentrations of a similar cation $Na^+$ as (NaCl) are shown in Figs. (35-37). It is obvious that the desorption of Cs(I) from different straw and sugarcane residue samples increases with increasing NaCl concentration. It could be observed that $10^{-1}$M NaCl elutes 51% of the loaded cesium from S.C sample, Fig.(35).

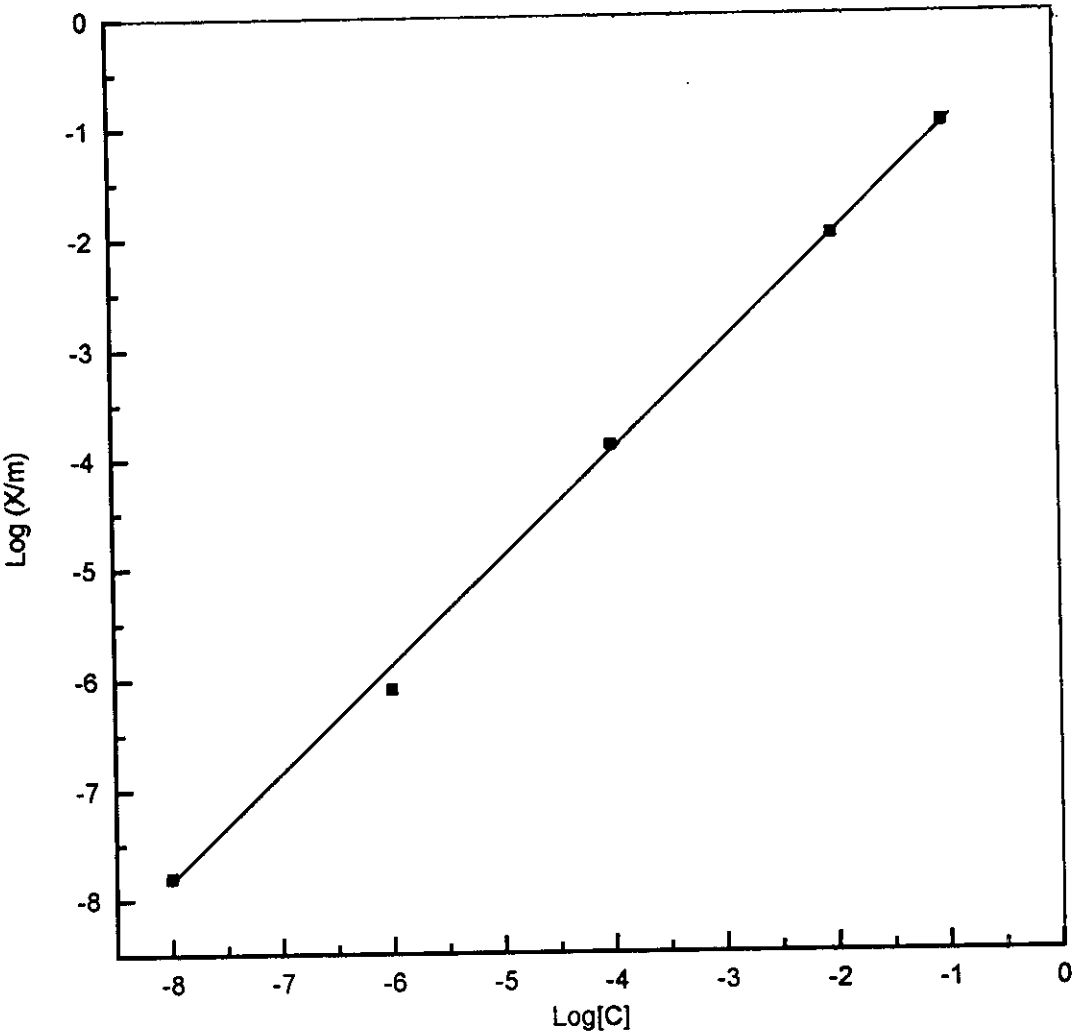

Fig.(33) Effect of carrier concentration on desorption of Cs(I) by R.S sample.

Using NaCl solutions of $10^{-2}$M and $10^{-3}$M reduces the desorbed percent to 35% and 30% respectively, Figs.(36 and 37).

Also, 47%& 45%& 44% of Cs(I) was leached from rice, wheat and maize straw samples respectively using $10^{-1}$M NaCl solution, as shown in Fig.(35). On increasing the contact time, a decreased of the amount of Cs(I) desorbed is observed, and this agrees with all the former cases.

### 3.7.5. Separation of Eu(III) from Cs(I):

A comparison of the sorption of Eu(III) and Cs(I) from distilled water of pH=5.2 by rice straw and sugarcane samples is plotted and represented in Fig.(38). It is clear that Eu(III) could be separated from Cs(I) from their mixture by straw and sugarcane samples after contact time of 80 min. by a series of successive experiments. So these natural cheap materials could not only adsorbs Eu(III) from distilled water without any chemical treatment but they could be used for separating Eu(III) from Cs(I) in their mixture. So, such natural materials find good application in radioactive waste fractionation.

### 3.8. Sorption studies of Eu(III), Co(II) and Cs(I) from their mixture:

Effect of pH variation on the sorption of Eu(III), Co(II) and Cs(I) from their mixture in sulfate solution have been studied on maize straw and sugarcane residue samples, Figs.(39 and 40). The maximum sorption of Eu(III), Co(II) and Cs(I) present in the mixture on maize straw sample from sulfate solution of pH=3.2 reaches 51%, 6.7% and 1.5% respectively. While the maximum uptake of Co(II) and Cs(I) at pH=4.8 reaches 5.2% and 39.1% on maize straw sample respectively. Also, the

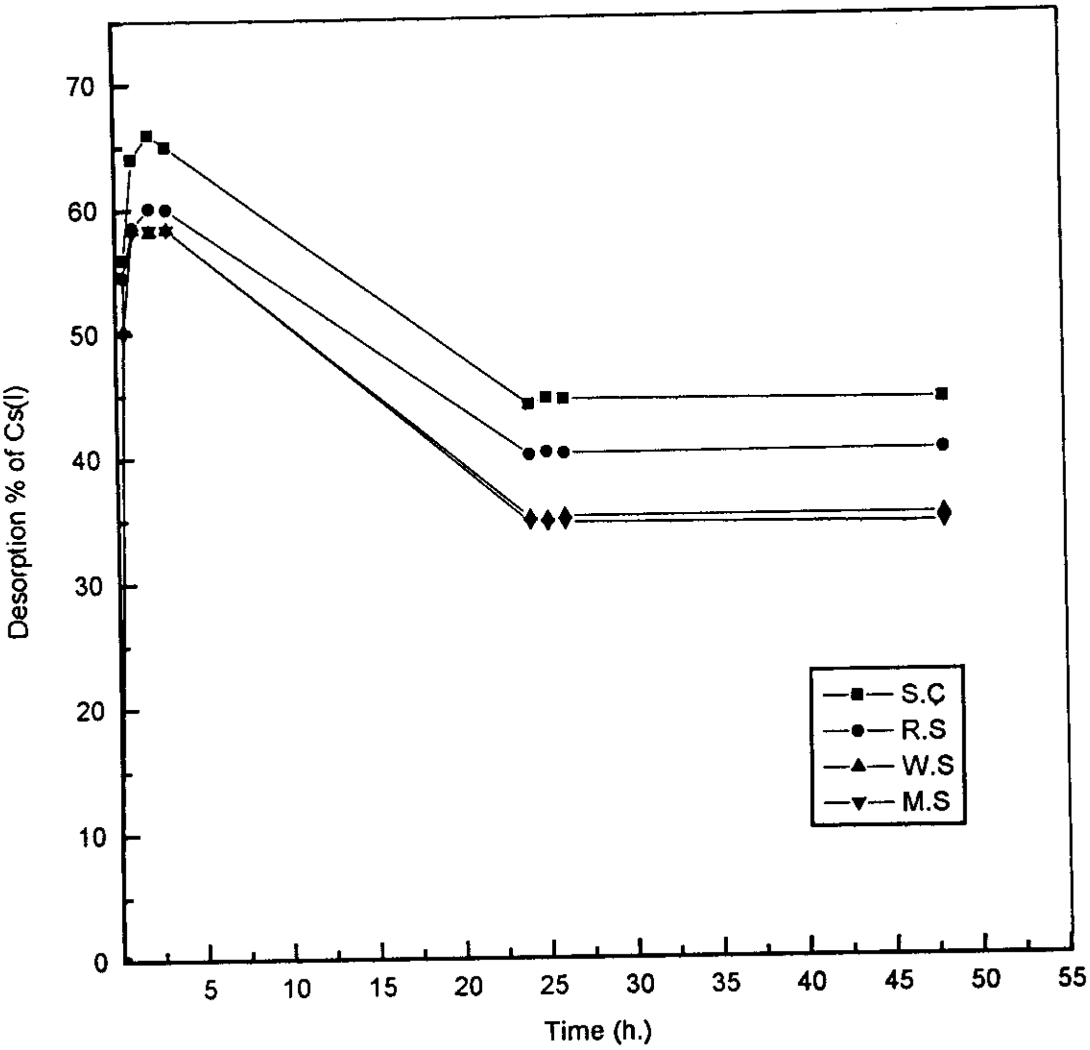

Fig.(34) Effect of contact time on desorption of Cs(I) from R.S, W.S, M.S& S.C samples using $H_2O$.

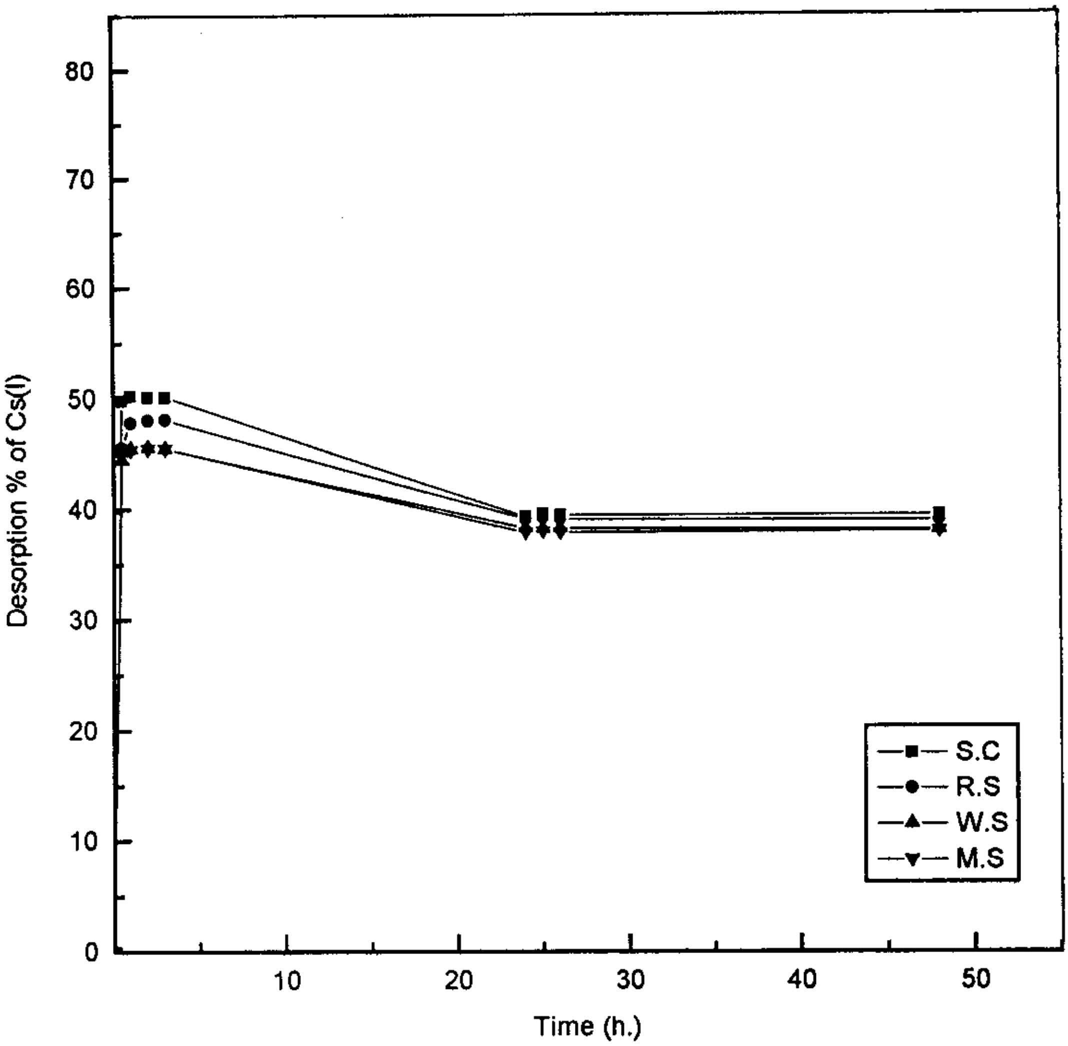

Fig.(35) Effect of contact time on desorption of Cs(I) from R.S, W.S, M.S& S.C samples using 0.1M NaCl.

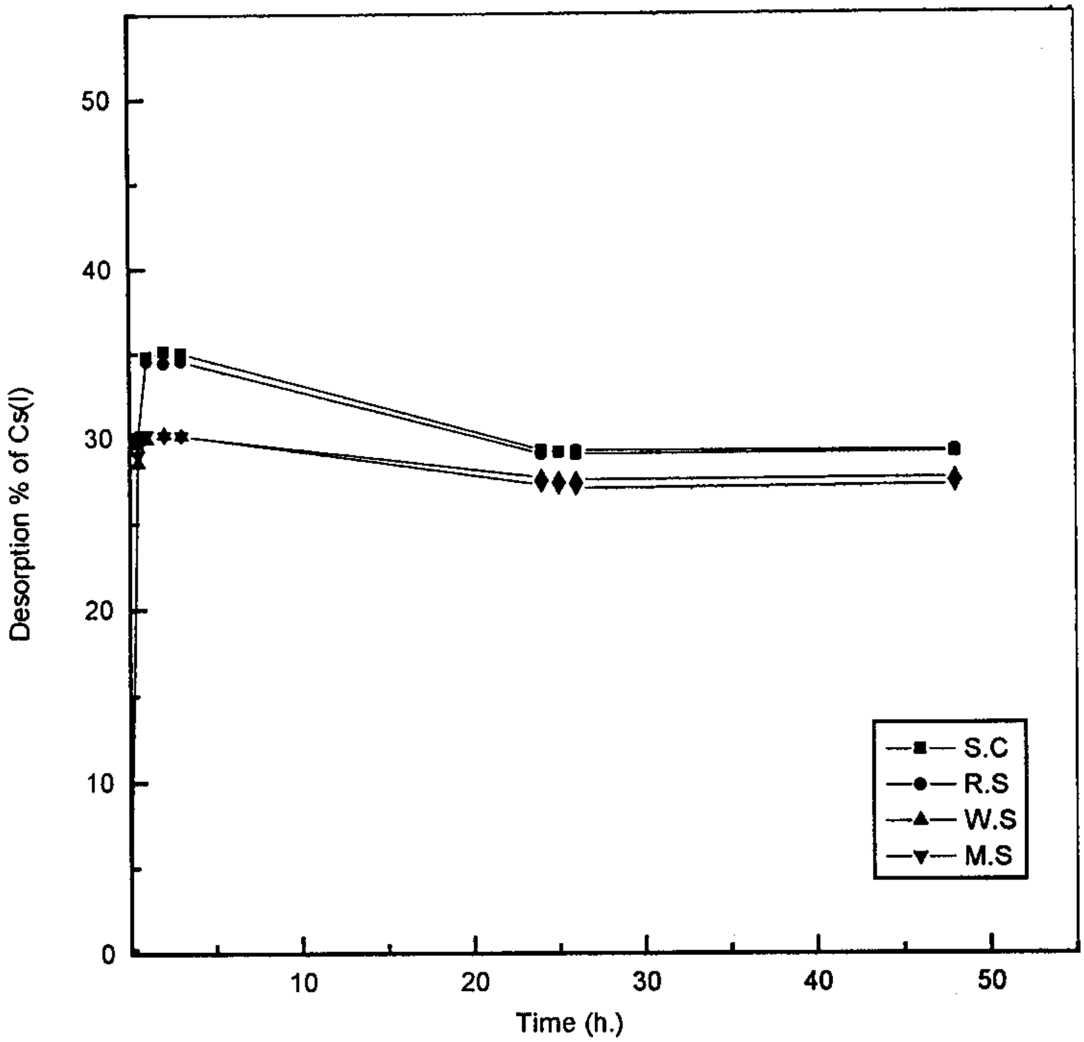

Fig.(36) Effect of contact time on desorption of Cs(I) from R.S, W.S, M.S& S.C samples using 0.01M NaCl.

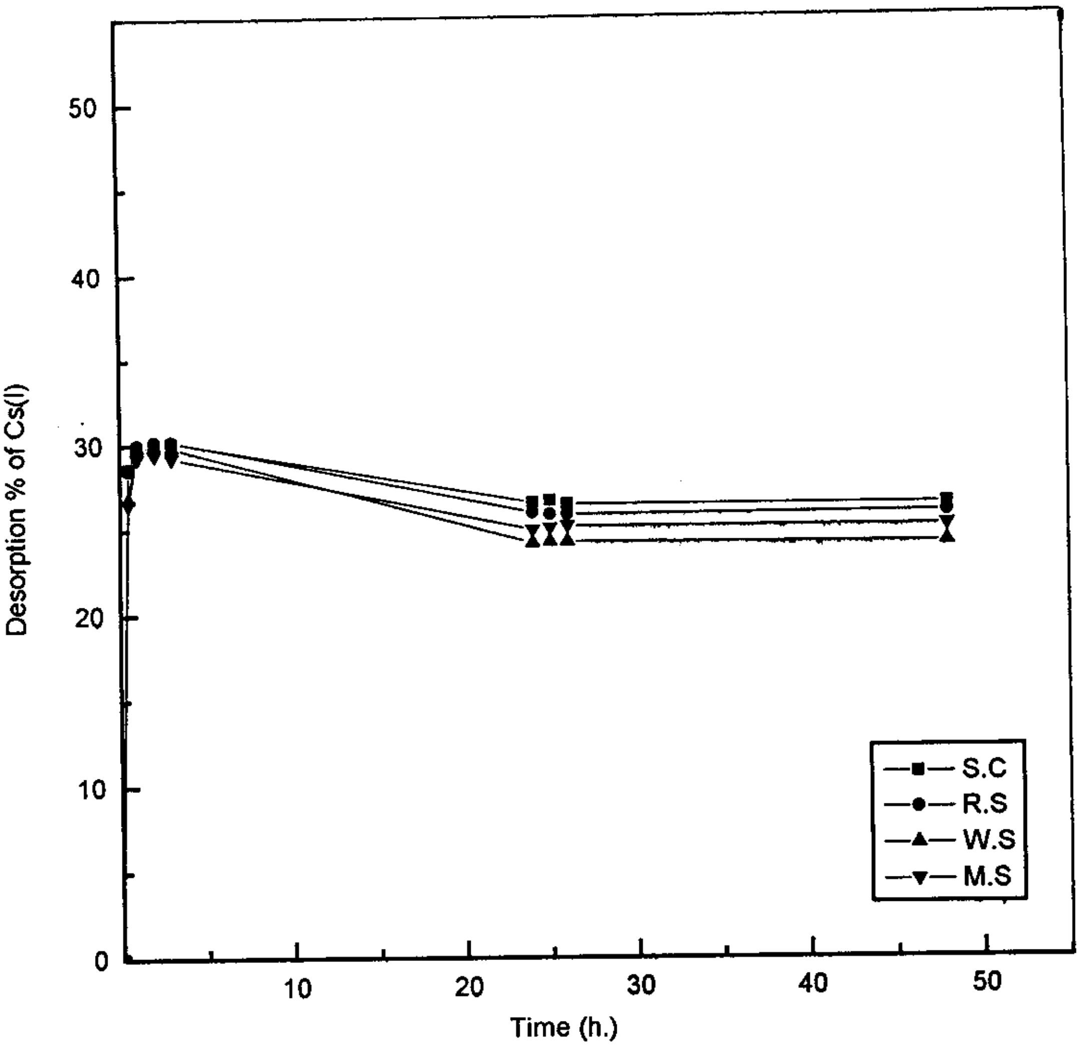

Fig.(37) Effect of contact time on desorption of Cs(I) from R.S, W.S, M.S& S.C samples using 0.001M NaCl.

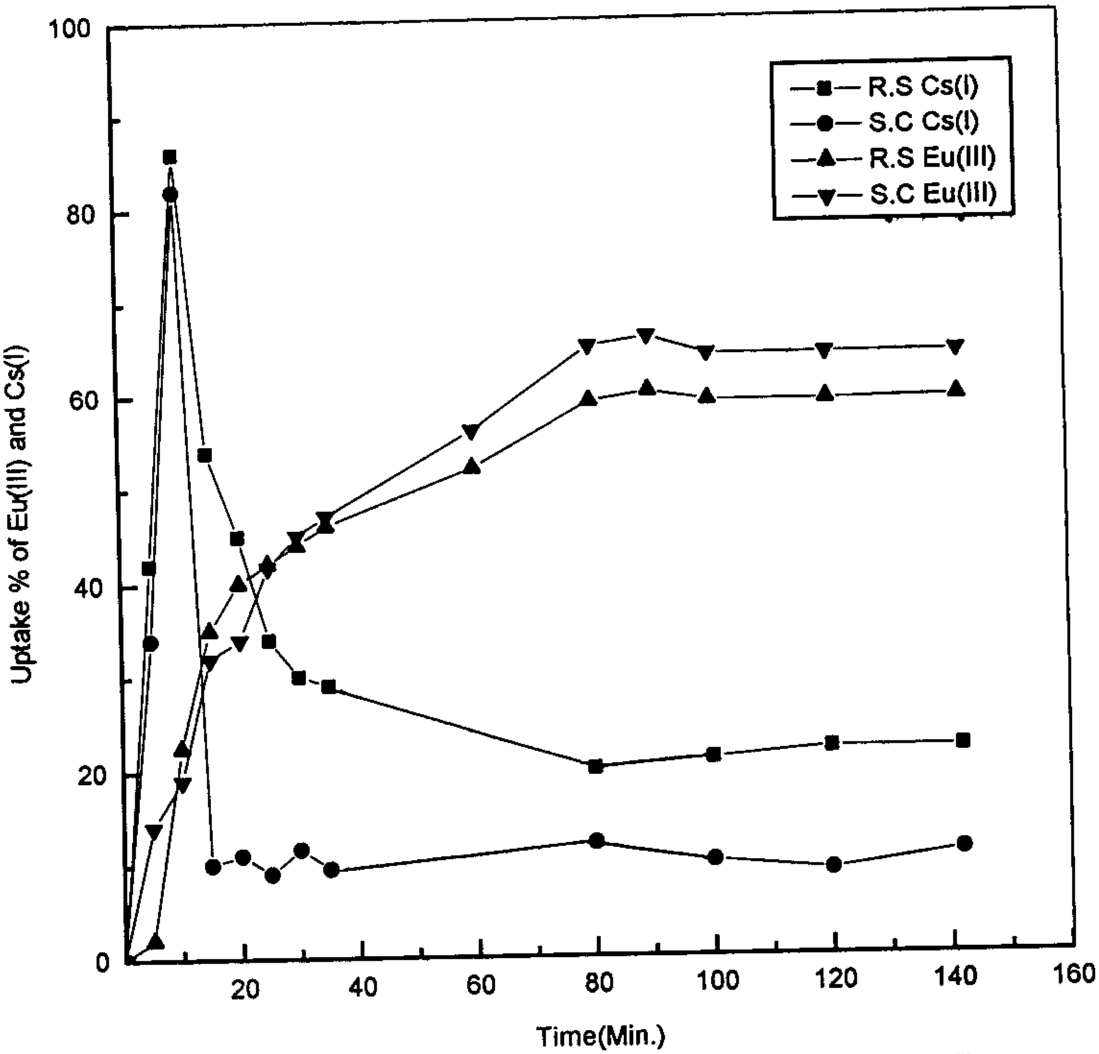

Fig.(38) Effect of contact time on adsorption of Eu(III) and Cs(I) from their mixture in distilled water of pH=5.2 using rice straw and sugarcane samples.

uptake % of Cs(I) on maize straw sample at pH=7.2 reaches 48.5%, Fig.(39). The same trend is also achieved for the sorption of the three studied radionuclides from their mixture on sugarcane samples, Fig.(40). From this figure it is obvious that maximum sorption of Eu(III), Co(II) and Cs(I) at pH=3.2 reaches 39.9%, 7.3% and 1.7% respectively. While sorption of Co(II) and Cs(I) at pH=4.8 reaches 4.6% and 35.9% respectively. Also, the sorption of Cs(I) on sugarcane residue sample at pH=7.2 reaches 47.3%. The data in Figs. (39 and 40) shows very close similarity of the capacity of maize straw and sugarcane residue for sorpting the studied elements from their mixture.

Sorption of the three radionuclides from their mixture in sulfate solution of pH=3.5 have been studied for sugarcane, maize, wheat and rice straw samples, Fig.(41). The data of this experiment shows that the uptake % of Eu(III), Co(II) and Cs(I) reaches 46.46%, 21.65% and 1.4% respectively on rice straw sample. Their uptake % reaches 48.17%, 19.39% and 1.32% respectively on wheat straw sample. While, it reaches 39%, 14.85% and 2.35% respectively on maize straw sample. Also, it reaches 34.8%, 7.02% and 1.21% respectively on sugarcane residue sample. Comparing these results with that obtained earlier for each element alone shows that the uptake of either elements is decreased from 80% to 46.46%, 57.5% to 21.65% and from 7.1% to 1.4% respectively on rice straw sample. Such decrease may be attributed to the competition between the cations for attacking the replacable active sites of the powdered straw. And this behavior occurs also for wheat, maize and sugarcane residue samples. These results indicate that Cs(I) show very low significant adsorption from the mixture. Hence cesium could be separated from the bulky solutions by adjusting the pH ≥ 7, which increases its uptake to 49.6% and 38% on rice straw and sugarcane samples respectively.

On the basis of the obtained data, it is clear that europium could be reasonably separated from cobalt and cesium at pH=3.5 from sulfate solution by sorption on different straw and sugarcane samples. Different separation factors of Eu(III), Co(II) and Cs(I) from each others are listed in table (12). Maximum values reached for the separation factors $D_{Eu(III)}$ / $D_{Cs(I)}$ and $D_{Co(II)}$ / $D_{Cs(I)}$ are 38.35 and 17.89 at pH=3.5 for rice straw sample respectively. Also, maximum value reached for the separation factor $D_{Eu(III)}$ / $D_{Co(II)}$ is 6.98 for maize straw sample at pH=3.2, where it reaches 7.8 for the separation factor $D_{Cs(I)}$ / $D_{Co(II)}$ for sugarcane sample at pH=4.8. The values of the separation factor between the neighboring pairs of metal ions are large enough to attain a feasible separation for these ions. Such separation factors are calculated by using the uptake % of each element obtained under the same experimental condition. This approach is in fact not the precise way for calculating the separation factors although it gives a very acceptable idea to the direction and possibility of separating the studied elements from a waste on environment containing the mixed together. So, it can be deducted that the used sorbent (i.e., straw samples) will be one of the materials to be used in the reprocessing of nuclear fuel. With repeating the separation experiments several times under the same conditions, the enrichment of the studied elements could be achieved.

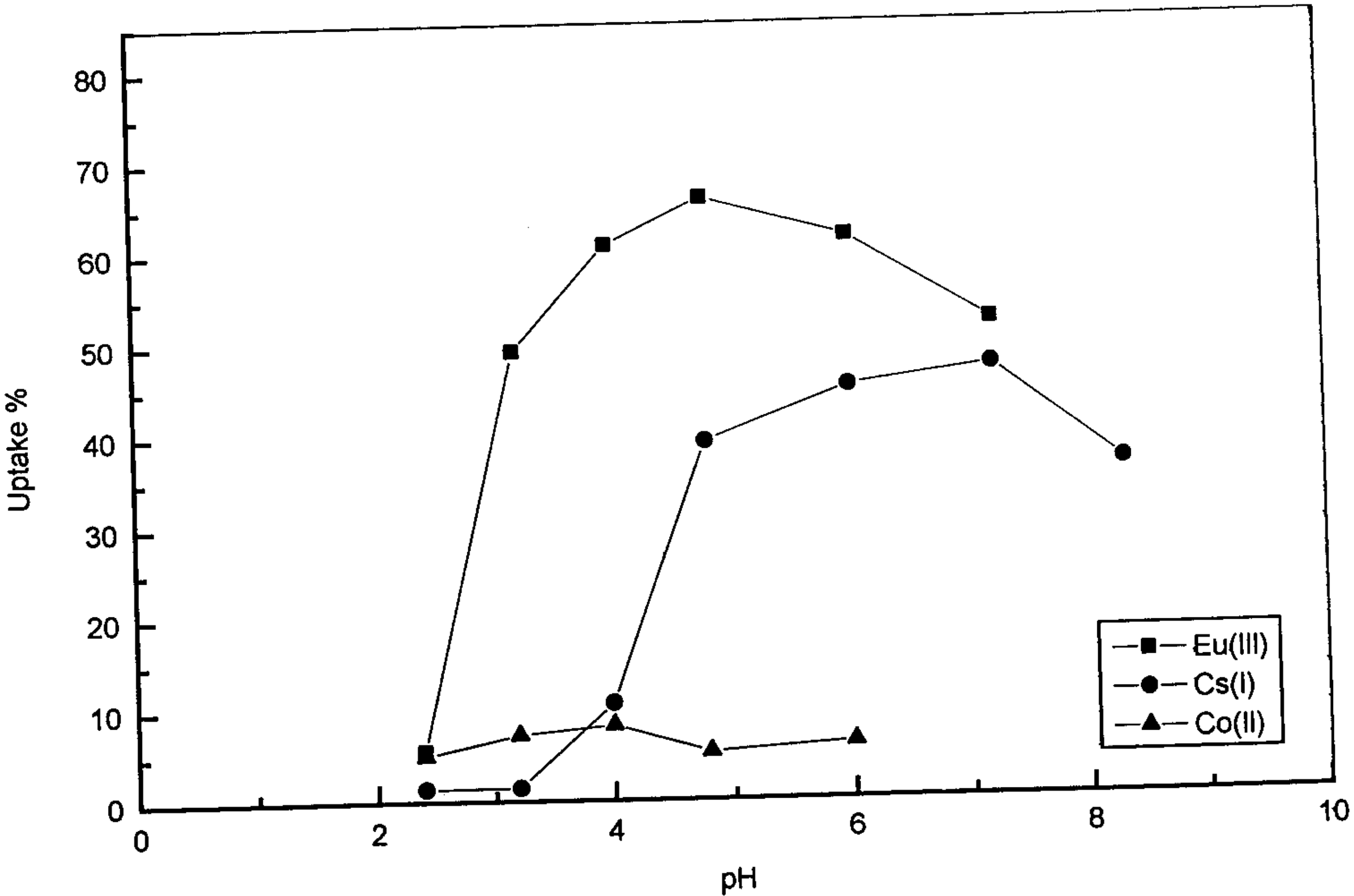

Fig.(39) Effect of pH on sorption of Eu(III), Co(II)& Cs(I) on maize straw sample (M.S) from their mixture in sulfate solution.

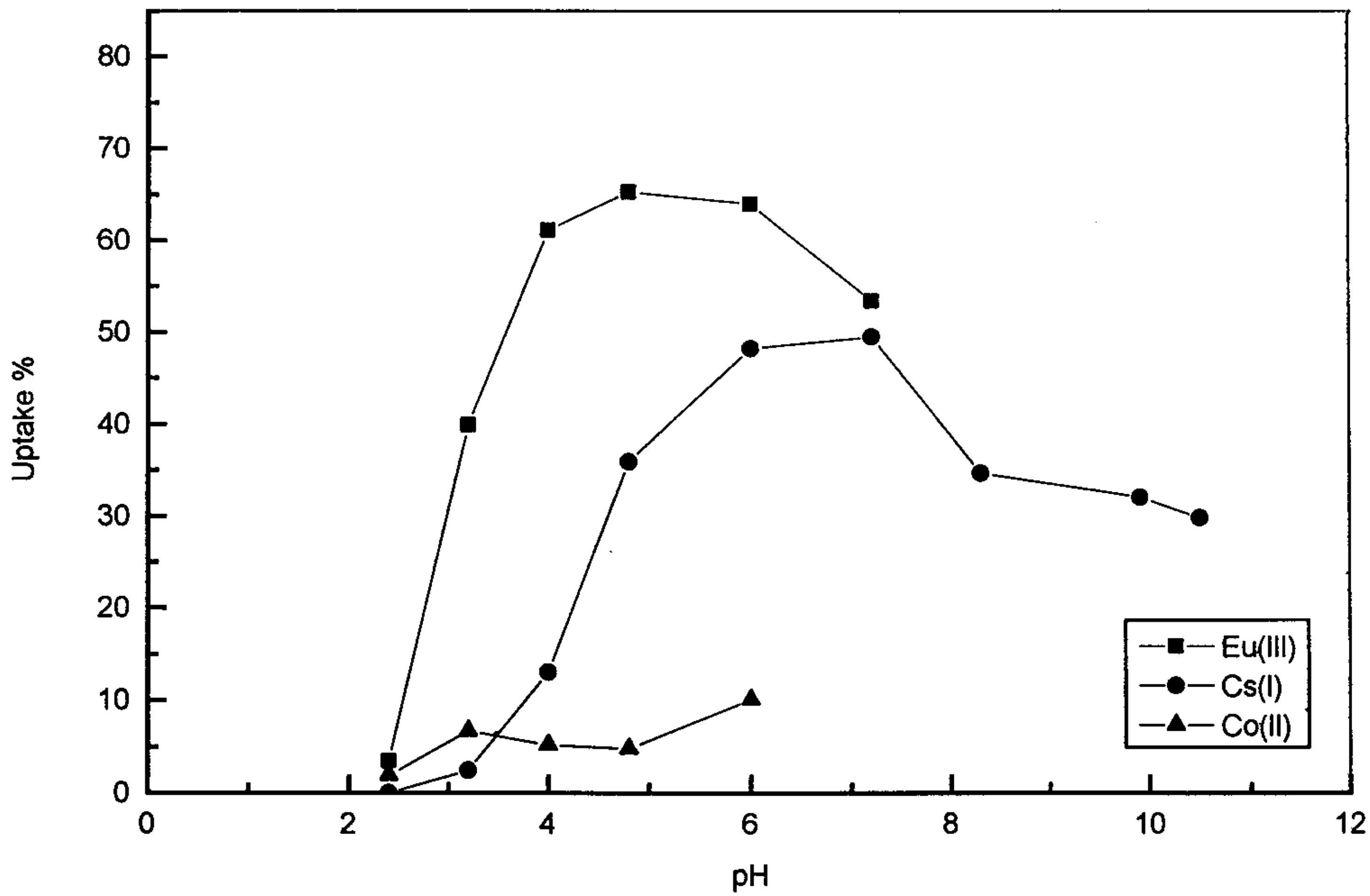

Fig.(40) Effect of pH on sorption of Eu(III), Co(II)& Cs(I) on sugarcane sample (S.C) from their mixture in sulfate solution.

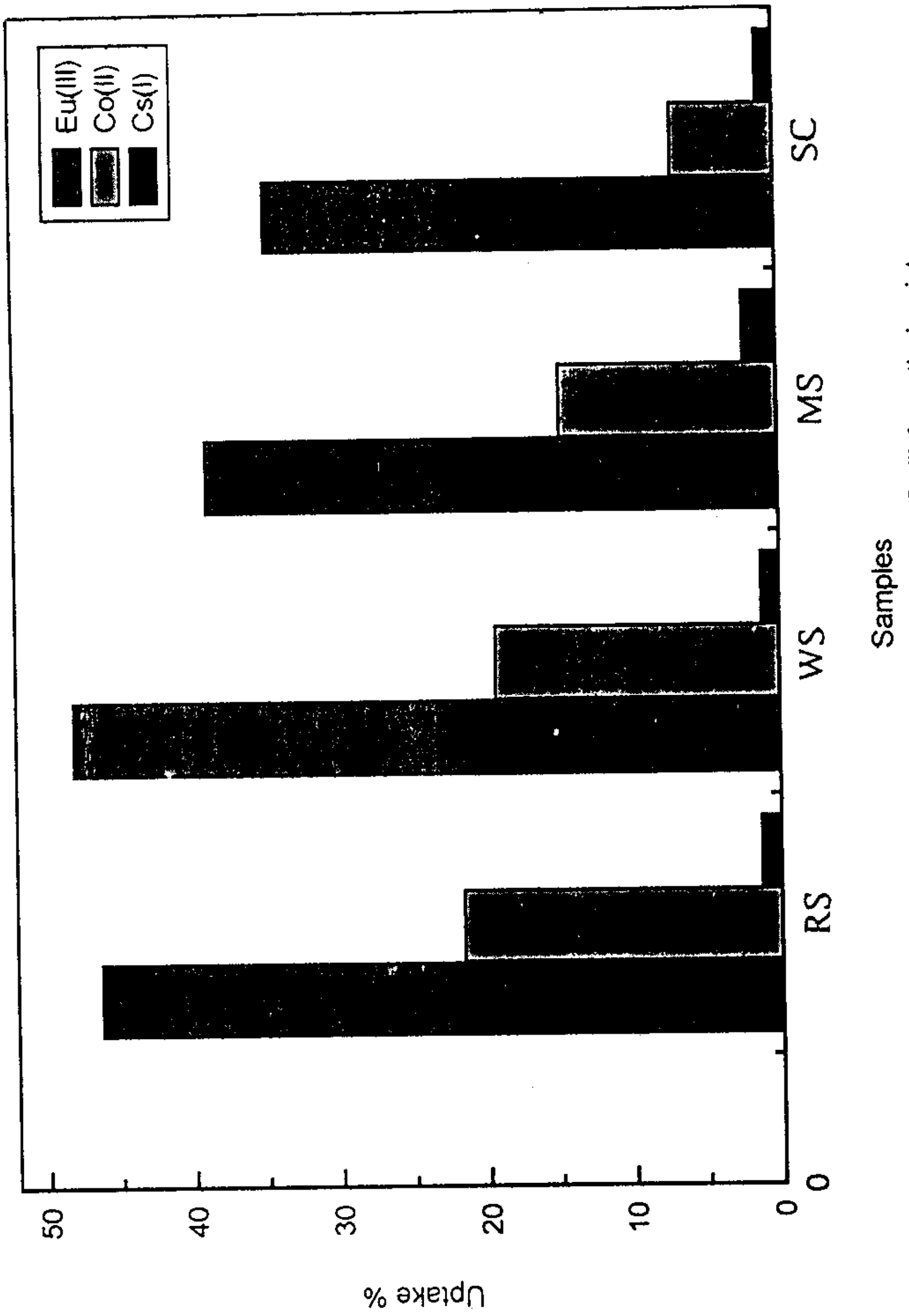

Fig.(41) Sorption of Eu(III), Co(II) and Cs(I) from their mixture in sulfate solution of pH=3.5 using different kinds of straw and sugarcane residue samples.

Table(12) **Separation factors for Eu(III), Co(II) and Cs(I) from their mixture in sulfate solution using different straw and sugarcane residue samples:**

| Separation factor | pH | Sugarcane (SC) | MaizeStraw (MS) | Wheat Straw (WS) | Rice Straw (RS) |
|---|---|---|---|---|---|
| $D_{Eu(III)} / _{Co(II)}$ | 3.5 | 4.96 | 2.63 | 2.48 | 2.14 |
| $D_{Eu(III)} / _{Co(II)}$ | 3.2 | 5.47 | 6.98 | ND | ND |
| $D_{Eu(III)} / _{Cs(I)}$ | 3.5 | 31.63 | 16.60 | 36.49 | 38.35 |
| $D_{EU(III)} / _{CS(I)}$ | 3.2 | 23.47 | 26.0 | ND | ND |
| $D_{Co(II)} / _{Cs(I)}$ | 3.5 | 6.38 | 6.32 | 14.69 | 17.89 |
| $D_{Co(II)} / _{Cs(I)}$ | 3.2 | 4.29 | 3.27 | ND | ND |
| $D_{Cs(I)} / _{Co(II)}$ | 4.8 | 7.80 | 7.52 | ND | ND |

ND: Not detected

### 3.8.1. The desorption studies of Eu(III), Co(II) and Cs(I) from their mixture:

Results of the effect of contact time on desorption of the elements in mixture Eu(III), Co(II) and Cs(I) from sugarcane residue sample using $10^{-1}$M $MnCl_2$ solution, at different pH values are shown in Figs.(42-47). The desorption of Eu(III), Co(II) and Cs(I) from sugarcane at pH=2.4 is 22%, 47% and 100% respectively after 3h. shaking time, Fig.(42). The plots in Fig.(43), represent the desorption of mixture at pH=3.2 using $10^{-1}$M $MnCl_2$. It is obvious that 20%, 17% and 92% of Eu(III), Co(II) and Cs(I) respectively were eluted after 3h. shaking time. Shaking for more than 24 hours does not affect the amount of each element eluted. At pH=4, Fig.(44), it could be observed that $10^{-1}$M $MnCl_2$ elutes 24% and 40% of the loaded Co(II) and Cs(I) respectively, but for Eu(III) partial precipitation occurs. At pH=4.8, the desorption of Co(II) and Cs(I) is 90% and 24.4% respectively, Fig.(45). The desorption of Co(II) and Cs(I) is 85% and 21.5% respectively at pH=6 after shaking time 3h., Fig.(46). At pH=7.2 the desorption of Co(II) and Cs(I) is 90% and 10% respectively after 3h. shaking time but for Eu(III) complete precipitation occurs (i.e, 100% of Eu(III) precipitated as $Eu(OH)_3\downarrow$), Fig.(47), where the precipitation of Eu(III) increases gradually with pH=4 to pH=7.2 until reaching complete precipitation (This precipitation is probably due to the formation of hydrolyzed species (as: $Eu(OH)_2^+$& $Eu(OH)^{2+}$).

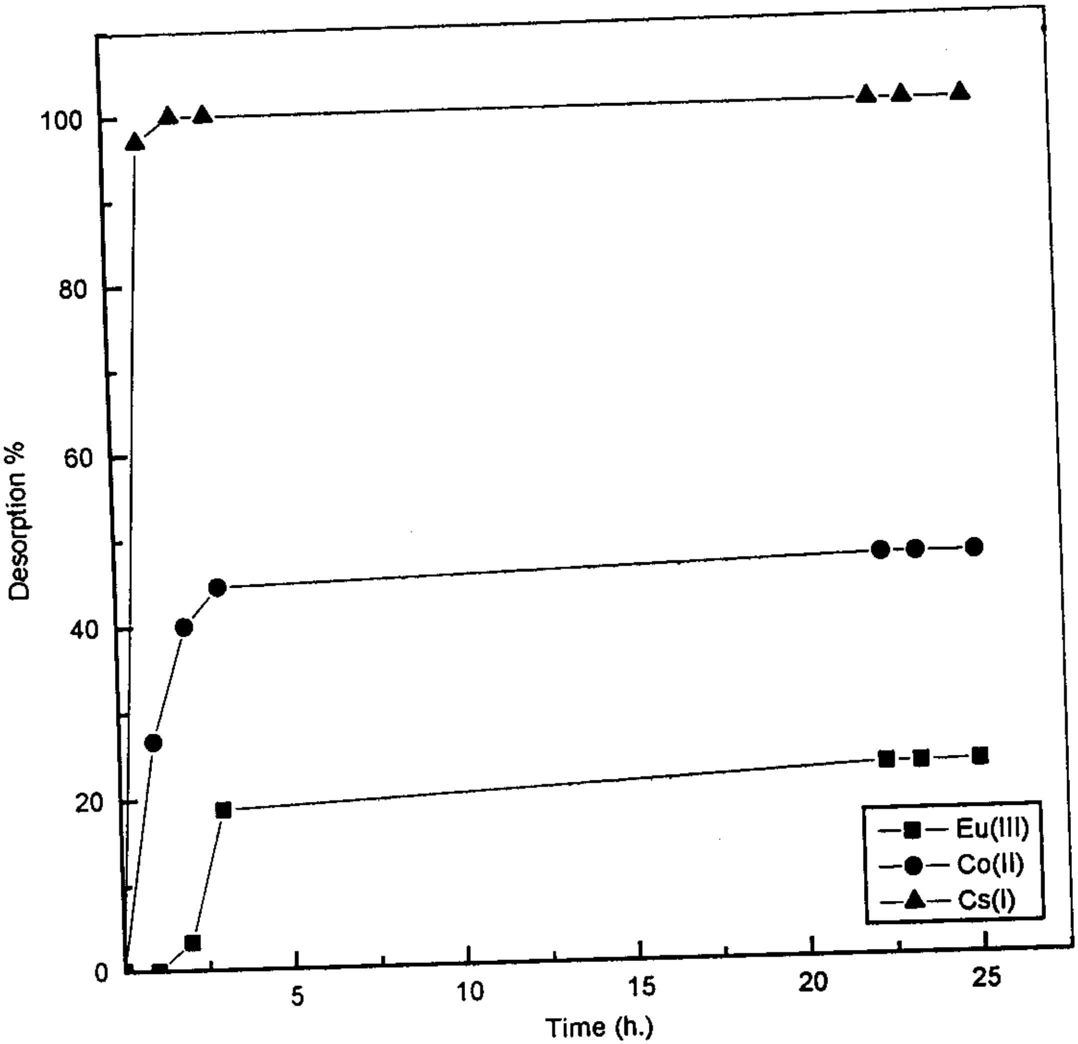

Fig.(42) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=2.4.

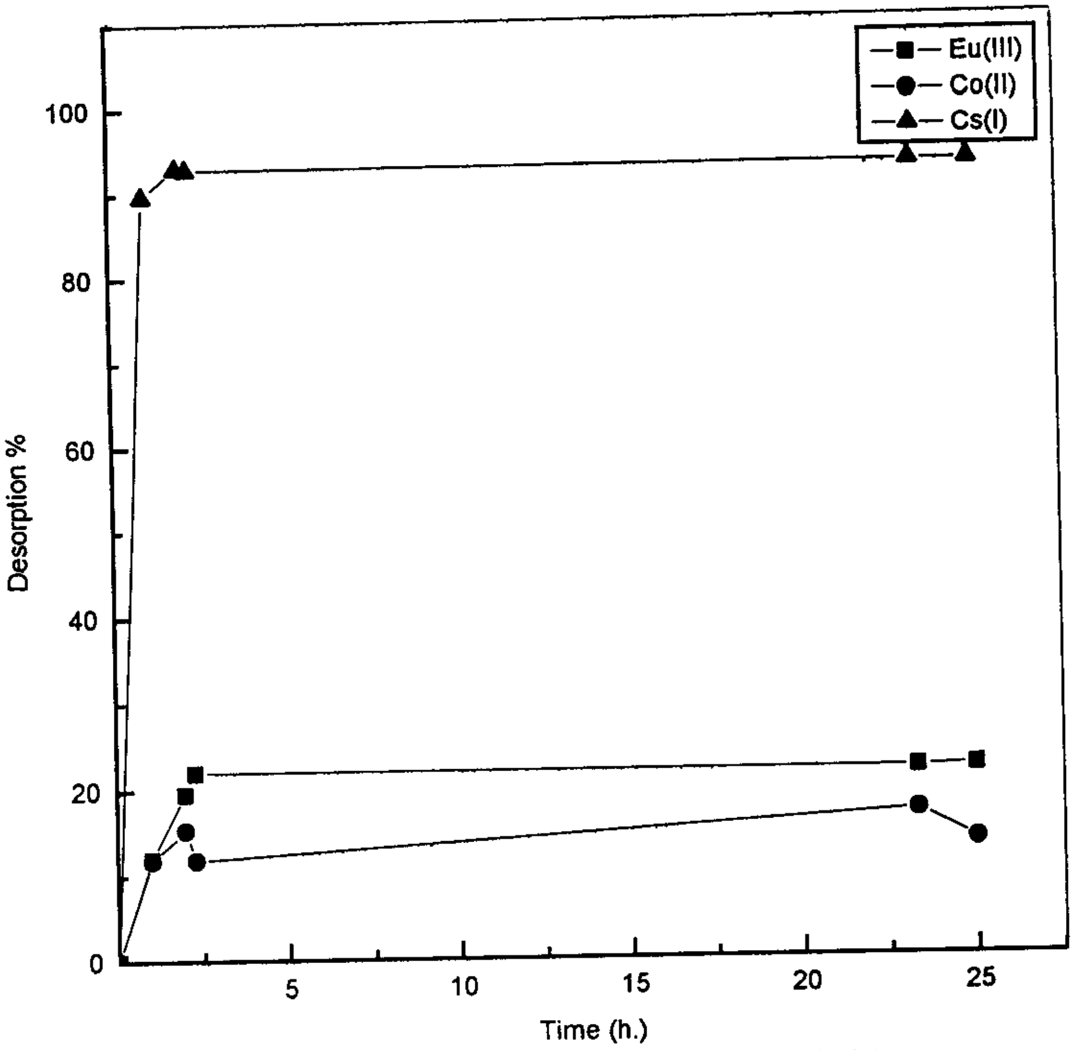

Fig.(43) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=3.2.

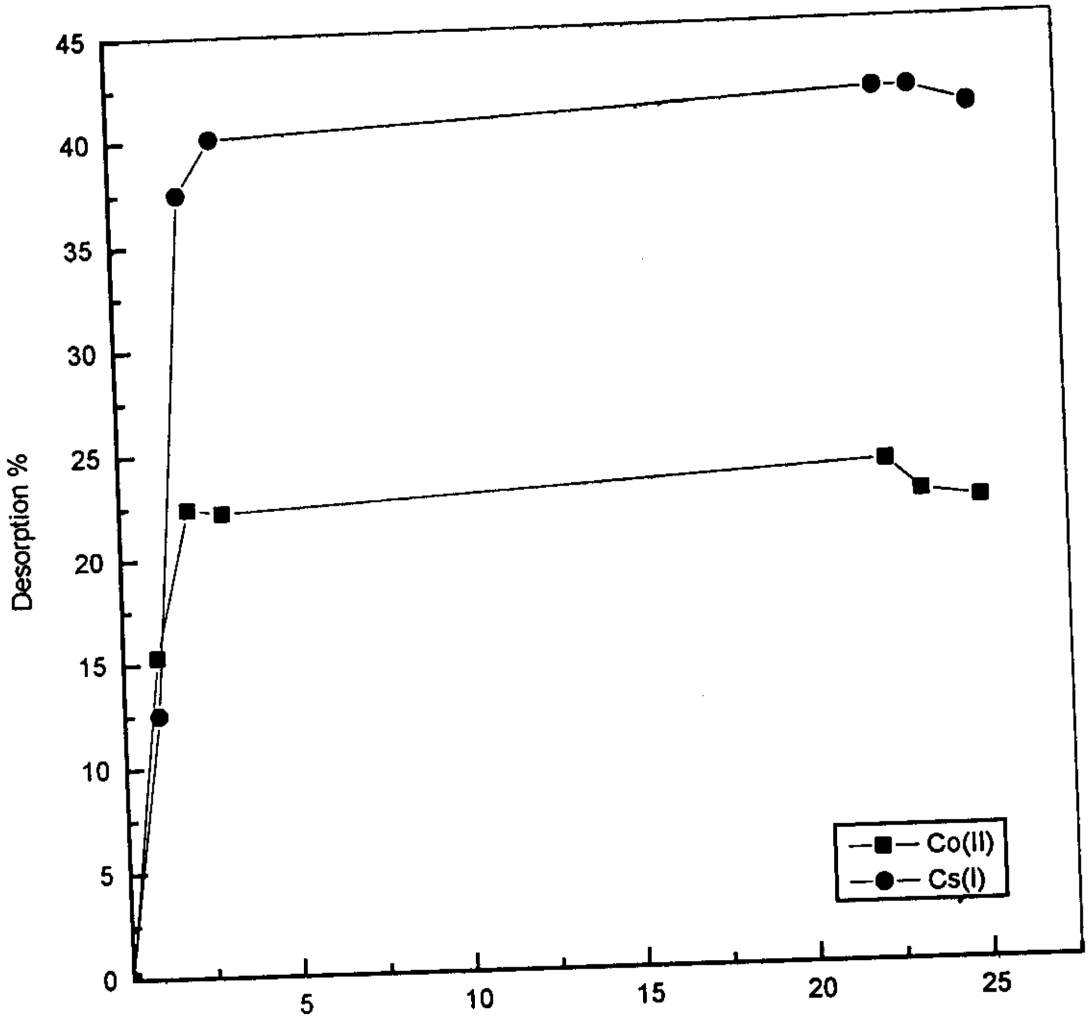

Fig.(44) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=4.

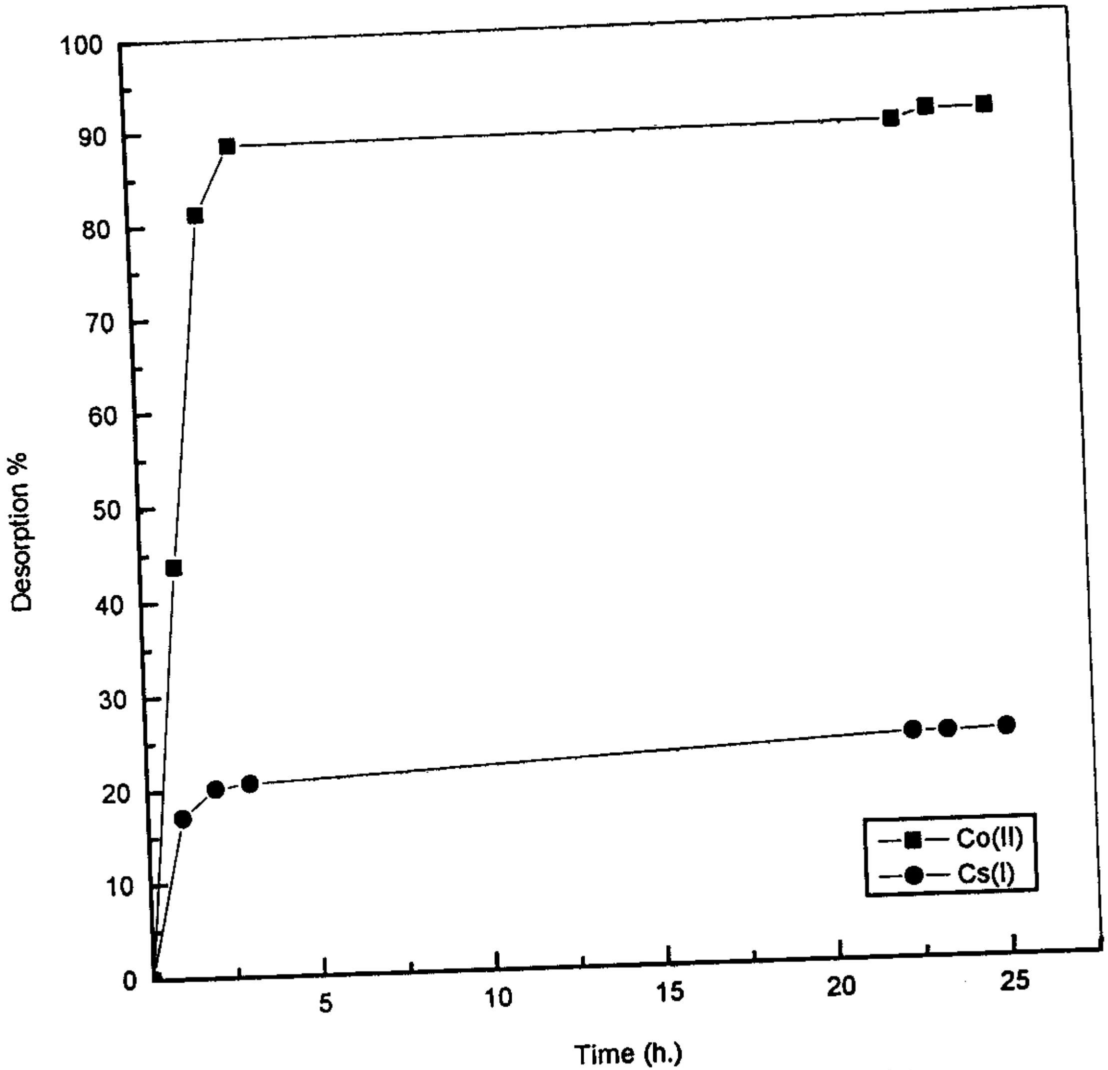

Fig.(45) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=4.8.

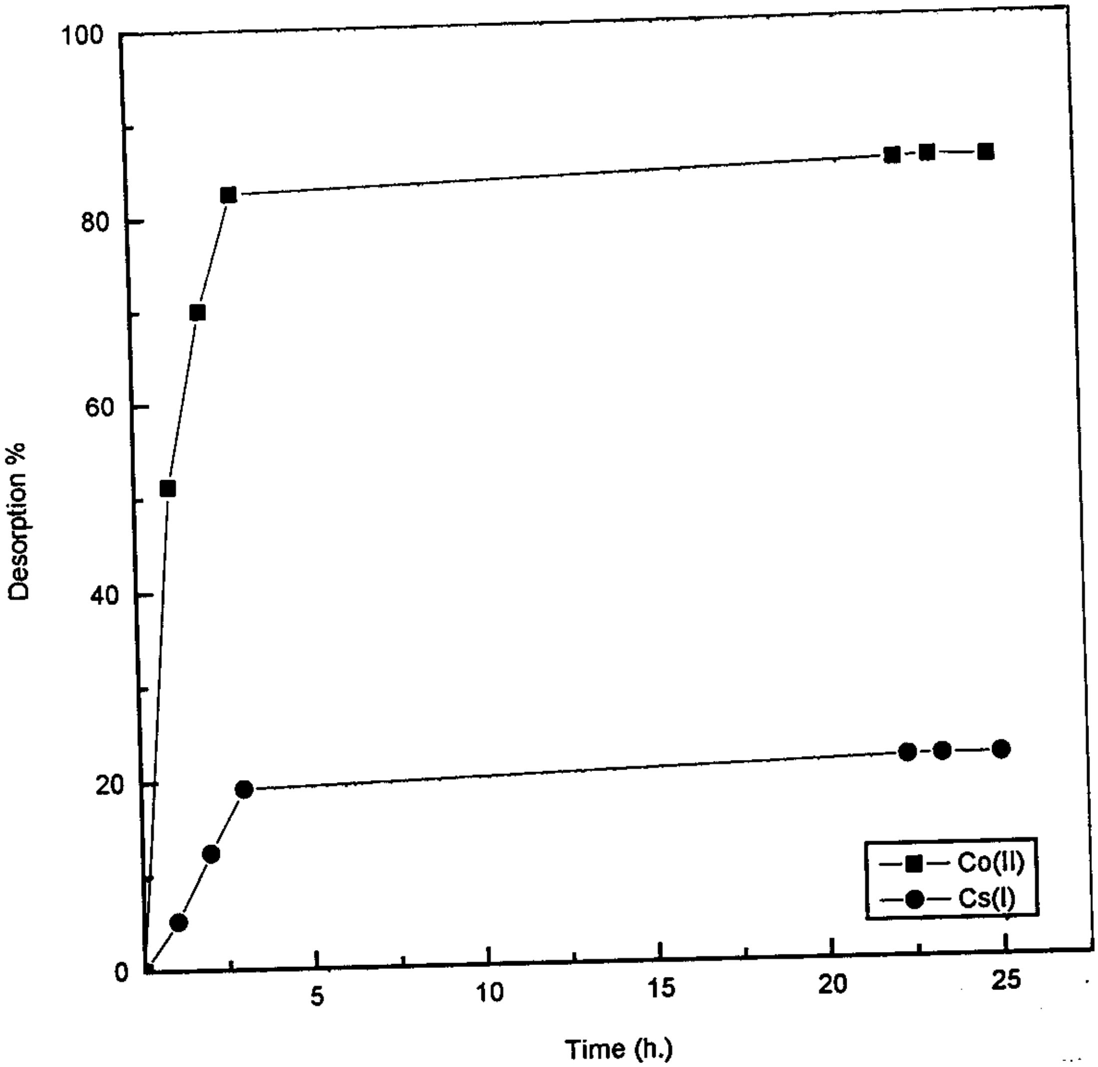

Fig.(46) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=6.

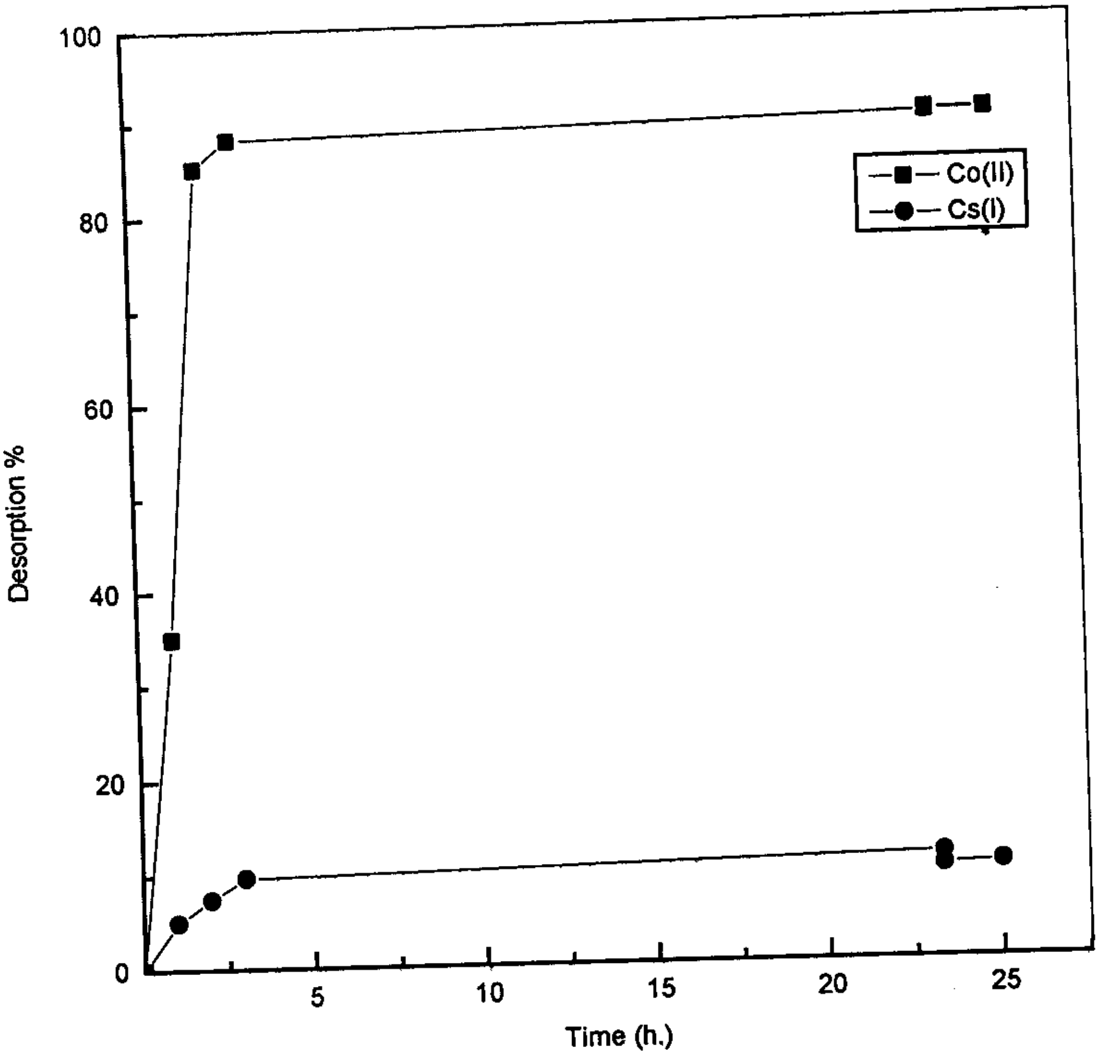

Fig.(47) Effect of contact time on desorption of mixture (Eu(III), Co(II)& Cs(I)) from S.C using 0.1M $MnCl_2$ at pH=7.2