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REMOVAL OF SOME ENVIRONMENTAL POLLUTANTS BY NATURAL MATERIALS USING RADIOMETRIC AND SPECTROPHOTOMETRIC TECHNIQUES

The paper deals with the adsorption of such pollutants as lead and cobalt by straw and sugar cane residues as the representatives of natural, cheap materials. Factors affecting the adsorption behaviour of the elements studied by different types of straw (rice, wheat and maize), in addition to sugar cane residue, were studied. These factors are as follows: pH, contact time, ion concentration and type of a medium. A trial of separating the elements tested from their mixture was undertaken and the results were discussed. Recycling experiments have been applied in order to adsorb and desorb lead from its media using straw and sugar cane samples. The success of reusing straw and sugar cane samples for further removal processes can lead to wide, practical applications of this technique in a semi-pilot plant for remediation or decontamination of pollutants from environmental wastes. Separation of Eu(III), Co(II) and Cs(I) radionuclides from their mixture has been tested. Radiometric and spectrophotometric analytic techniques are used in the present study.

1. INTRODUCTION

Recently, adsorption of some radionuclides by natural materials was investigated [1]–[4]. The use of cellulose materials and wood powder in adsorption of some radionuclides has been reported [5]–[7]. The retention of such elements as Np, Pu, Am, Sm, Zn and Cs which may exist in radioactive waste matrix has been carried out using clay and zeolite [8]. Certain plants as natural materials were used in order to adsorb and decontaminate some heavy metals in polluted water [9]. Straw pretreated with concentrated nitric acid has been used as an adsorbent in column [10]. It allowed separation of thorium from uranium and its daughters in the case of high absorbability and high affinity of the absorbent to thorium. In the present work, the studies of the adsorption of Pb(II) and Co(II) on different kinds of straw rice (RS), wheat (WS) and maize (MS) and sugar cane residues (SC) have been undertaken.

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2. EXPERIMENTAL

Different kinds of straw samples (rice, wheat and maize) were collected in dry manner after harvest seasons. All the samples collected were air-dried and then placed in an oven for two hours at 110 °C to assure complete drying. The straw samples were mechanically ground. The fraction having a diameter of 0.63 mm was selected. All the samples selected were used without any chemical treatment. Batch experimental technique was applied in the present study. 10 cm^3 of aqueous solution containing the elements tested was shaken mechanically with 0.1 g of the straw or sugar cane residue sorbent sample. Then the solution was centrifuged using a centrifuge with 5000 r.p.m. for 10 minutes in order to obtain clear and single-phase solution. Two cm^3 of the solution obtained were subjected to elemental analysis. Radiometric determination was applied in order to identify radioactive isotopes used in the present work. Highly pure germanium detector (HPGe) connected to a nucleus computerized multichannel analyzer of the Genie-2000 Canberra type was used. Such radioisotopes as $^{152+154}Eu$, ^{60}Co and ^{137}Cs were used to trace their corresponding elements. The lead content in the aqueous solution was measured spectrophotometrically (measurement of absorbance at the wavelength of 430 nm), using a spectrophotometer of the 340 Perkin Elmer type. The V/m ratio of a value of 100 cm^3/g was maintained unvaried for all experiments; V is the volume of the solution used, and m is the mass of the absorbent sample. All the experiments were carried out at a room temperature of 25 °C ±2. The adsorption efficiency is calculated from the following equation [14]:

$$\text{adsorption efficiency} = \frac{A_0 - (A_t + A_w)}{A_0 - A_w} \times 100,$$

where:

A_0 – the initial radioactivity of the aqueous solution,
A_t – the final radioactivity of the aqueous solution at the time t,
A_w – the radioactivity of the adsorbate on the walls of the tube.

3. RESULTS AND DISCUSSION

The results obtained in the present work are summarized and discussed in the following sections.

3.1. SORPTION OF Pb(II)

Factors affecting adsorption of lead on straw and sugar cane samples can be itemized as follows: pH, contact time, element concentration and competing ion concentration. The results of the effect of pH variation on the adsorption of lead on sugar cane residue sample are shown in figure 1. As shown in this figure, 90% adsorption of Pb(II) is achieved at pH = 5 after about 3 hours of shaking and at an initial lead concentration of 10 ppm. Also, 97% of lead is adsorbed at pH = 5 and at an initial lead concentration of 100 ppm.

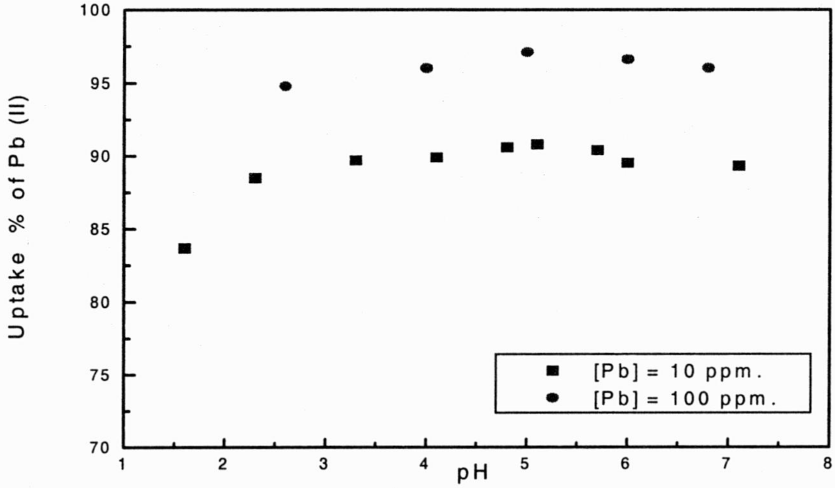

Fig. 1. Effect of pH on adsorption of Pb(II) on sugar cane residue sample

Figure 2 shows the effect of contact time on adsorption of Pb(II) on different straw and sugar cane samples from nitrate solution at pH = 5. Adsorption of Pb(II) reaches its maximum value of 97% for all the samples after about half an hour of shaking. So, an equilibrium time of half an hour for all the samples tested is accepted for all experiments.

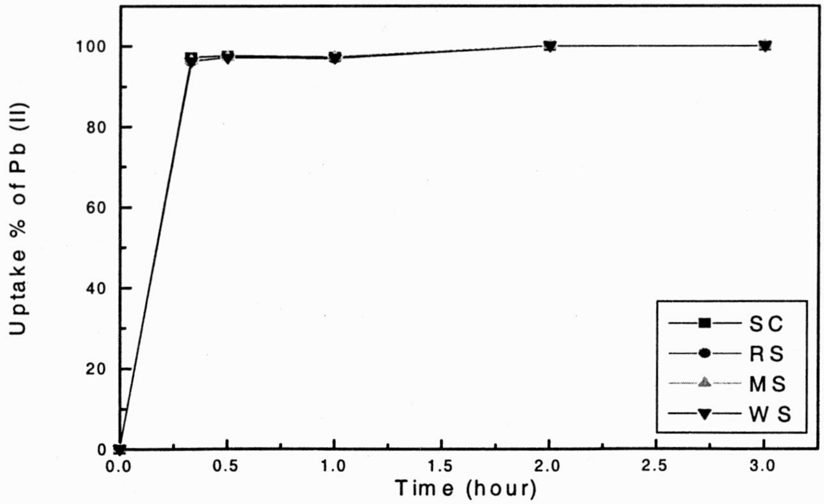

Fig. 2. Effect of contact time on adsorption of Pb(II) on different straw and sugar cane residue samples

Adsorption isotherm of Pb(II) was plotted based on different concentrations of Pb(II) adsorbed on rice straw samples in nitrate solution. The amount of Pb(II) adsorbed per gram (X/m) in meq·g^{-1} is plotted against the Pb(II) concentration (C) in a logarithmic scale (figure 3). The plot in this figure is a straight line of a slope ~ 0.7. This linearity of the isotherm means that the adsorption process follows the Freundlich isotherm [7]. This means that the adsorption of Pb(II) cations on the rice straw samples takes place as a result of formation of a single monolayer of the ionic species being sorbed [11]. This finding agrees with that published for the adsorption of various metal ions on cellulose [12] and on wood powders [7], [13].

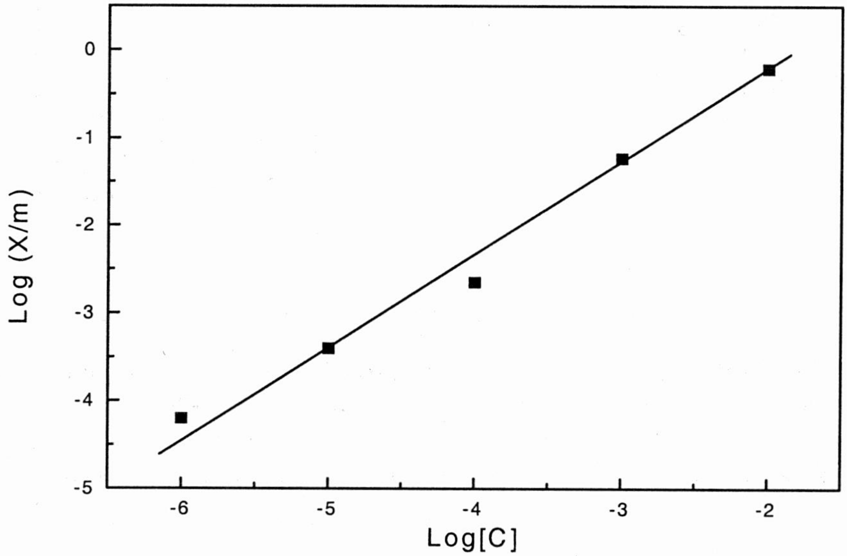

Fig. 3. Effect of lead ion concentration on the adsorption of Pb(II) on rice straw samples

Figure 4 shows the effect of competing ion concentrations on the adsorption of Pb(II) on straw and sugar cane samples at pH = 5. Different concentrations of Ni(II) ions were obtained using different concentrations of the solutions of nickel chloride which was added to a solution of 4.83×10^{-3} M lead nitrate, and adjusting pH to 5. It is observed that with an increasing Ni(II) concentration the adsorption of Pb(II) decreases. The ionic radii of Pb(II), 1.37 Å, and Ni(II), 1.243 Å, are very close to each other and may affect the adsorption of Pb(II) on the samples tested in the presence of Ni(II) in the same solution.

Table 1 shows adsorption efficiency of Pb(II) from industrial wastewater sample collected from leather industries. The determined concentration of lead in the sample collected was 12.48 ppm. Maximum adsorption efficiency of Pb(II) reached 96.3% for sugar cane residue samples. This result encourages us to apply this technique in order to decontaminate the lead-polluted environment.

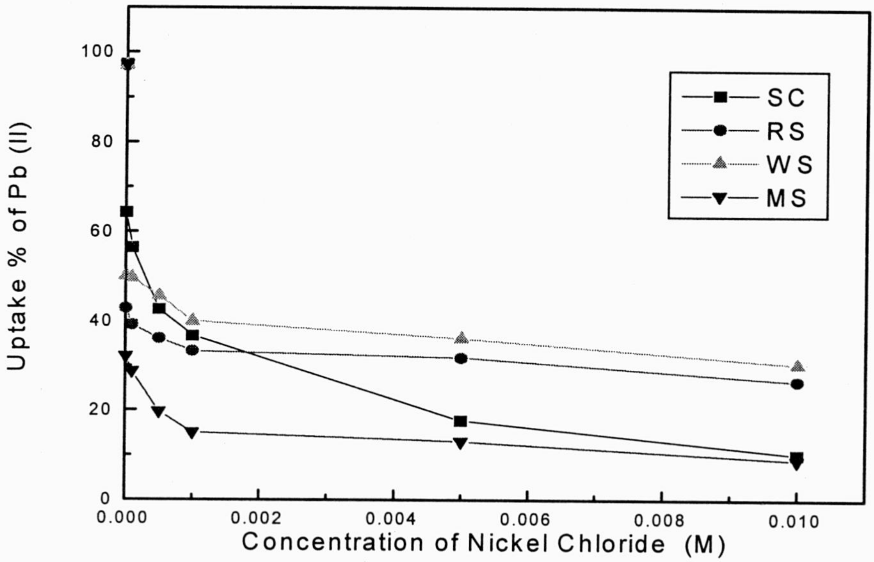

Fig. 4. Effect of competing ion concentration on adsorption of Pb(II) on different straw and sugar cane samples in $NiCl_2$ solution

Table 1

Adsorption of Pb(II) from industrial wastewater with an initial lead concentration of 12.48 ppm on different straw and sugar cane residue samples after one-hour shaking

Sample	Adsorption efficiency of Pb(II) (%)	Final Pb(II) concentration (ppm)
Sugar cane residue (SC)	96.3	0.46
Rice straw (RS)	94.5	0.67
Wheat straw (WS)	93.5	0.81
Maize straw (MS)	94.3	0.71

3.2. DESORPTION OF Pb(II)

Results of the effect of contact time on the desorption of Pb(II) from different straw and sugar cane residue samples using 0.1 M, 0.01 M and 0.001 M $MnCl_2$ solutions are shown in figures 5–8. $MnCl_2$ solutions have been chosen because of their previous successful use in similar studies [7], dealing mainly with cellulose structure as our natural material. The percent of desorption of Pb(II) from straw and sugar cane residue increases with increasing the $MnCl_2$ concentration. Maximum desorption of Pb(II) from sugar cane reaches 90% using 10^{-1} M $MnCl_2$ solution, as shown in figure 5. In 10^{-3} M solution of $MnCl_2$, only 25% of Pb(II) from the sugar cane residue sample are desorbed. Also, 90% of Pb(II) is leached from rice straw sample using 10^{-1} M of $MnCl_2$ solution, as shown in figure 6. The maximum desorption of Pb(II) from wheat and maize straw reaches 80%

using 10^{-1} M solution of $MnCl_2$, as shown in figures 7, 8. Desorption in distilled water has also been tested. No desorption is achieved in this case, and this means that distilled water is not suitable for leaching the Pb(II) adsorbed.

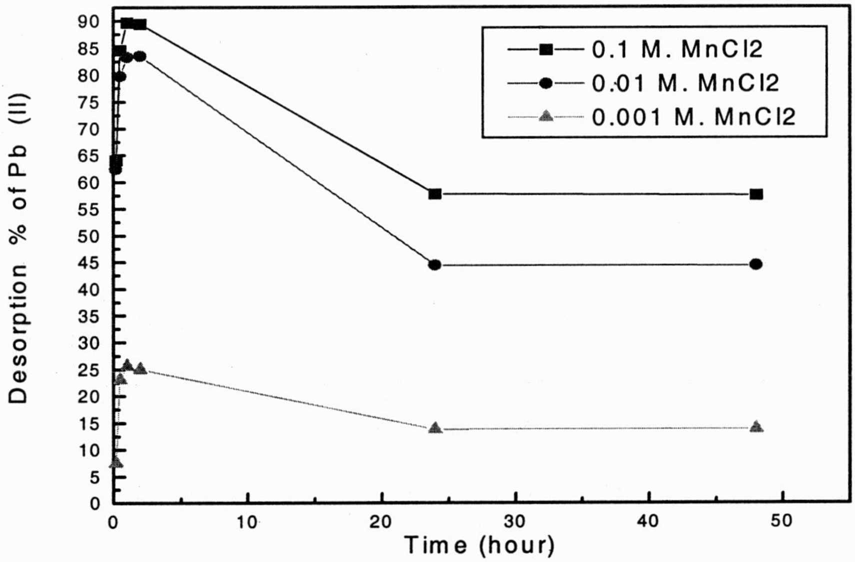

Fig. 5. Effect of contact time on desorption of Pb(II) from sugar cane residue samples in $MnCl_2$ solutions

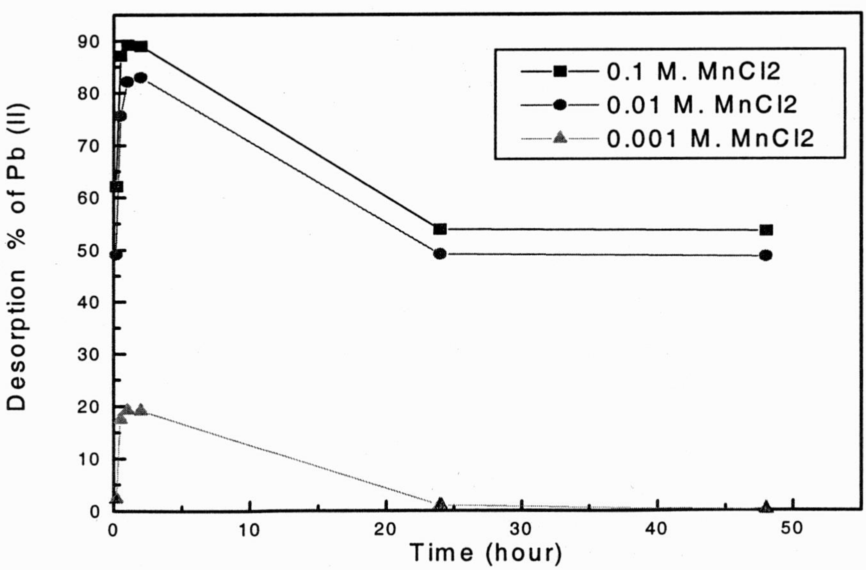

Fig. 6. Effect of contact time on desorption of Pb(II) from rice straw samples in $MnCl_2$ solutions

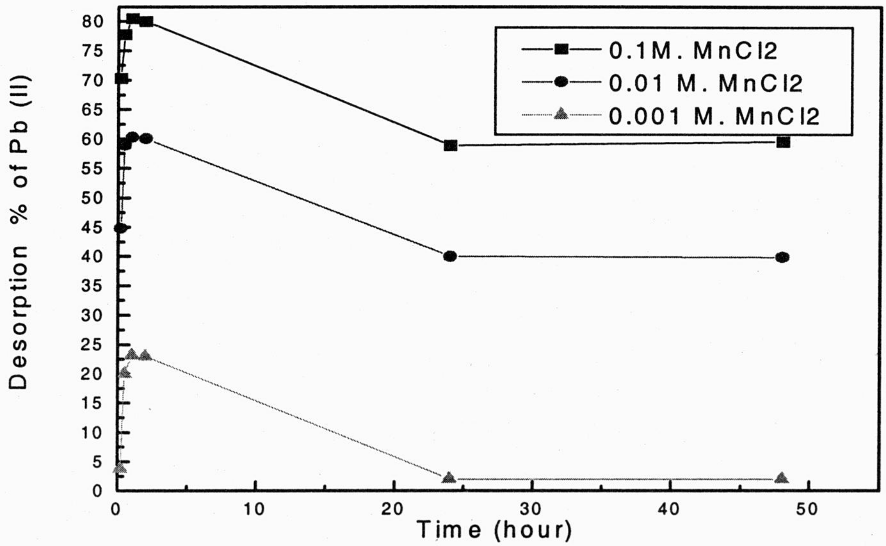

Fig. 7. Effect of contact time on desorption of Pb(II) from maize straw samples in $MnCl_2$ solutions

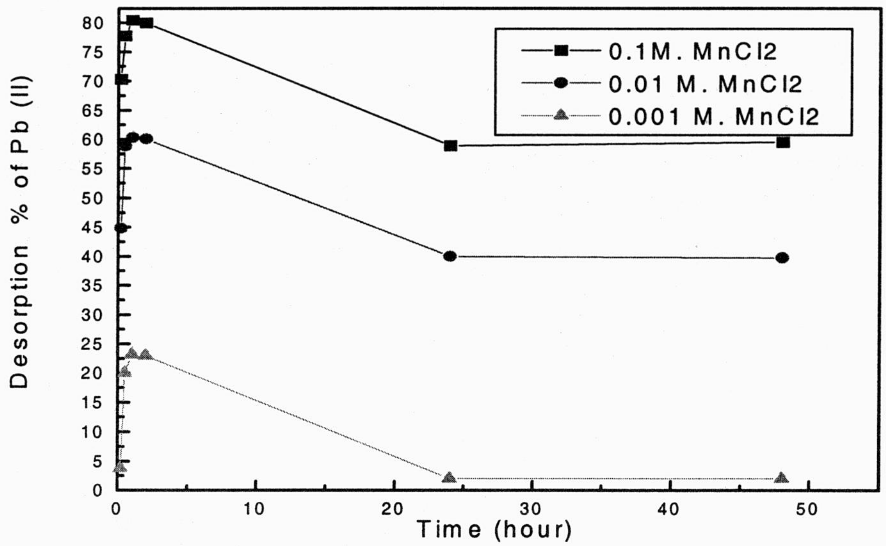

Fig. 8. Effect of contact time on desorption of Pb(II) from wheat straw samples in $MnCl_2$ solutions

3.3. ADSORPTION–DESORPTION RECYCLING OF Pb(II)

Table 2 shows the results of adsorption–desorption recycling of Pb(II) using nitrate solution of pH = 5 during the adsorption cycle and 10^{-1} M solution of $MnCl_2$

during the desorption cycle. Adsorption efficiencyof Pb(II) reaches 97.9% on rice straw (the first use of rice straw sample). Desorption of Pb(II) from RS sample using 10^{-1} M solution of $MnCl_2$ reaches 86.6% in the first desorption cycle. In the second desorption cycle, the desorption of Pb(II) reaches 99.4%. The rice straw sample from the last desorption cycle is reused for a new adsorption process of Pb(II) from nitrate media of pH = 5 (the second use of rice straw sample). The adsorption of Pb(II) in the second adsorption step reaches 95.8%. Shaking for each experiment lasts one hour. The same interpretation is given for the other straw and sugar cane residue samples.

Table 2

Adsorption and desorption of Pb(II) on different straw and sugar cane residue samples using nitrate media of pH = 5 and 10^{-1} M $MnCl_2$ in recycling steps, one hour-shaking for each step

Samples	Adsorption of Pb(II) (the 1st use of samples) (%)	Desorption of Pb(II) (the 1st cycle) (%)	Desorption of Pb(II) (the 2nd cycle) (%)	Adsorption of Pb(II) (the 2nd use of samples) (%)
Sugar cane	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

From these results it is clear that all the straw and sugar cane residue samples could be reused successfully for a very effective adsorption of Pb(II). Also, these samples could be cleaned off the adsorbed Pb(II) in two successive desorption steps. This result may encourage us to use regenerated straw in several recycling steps in a semi-pilot work for cleaning the environment off Pb(II).

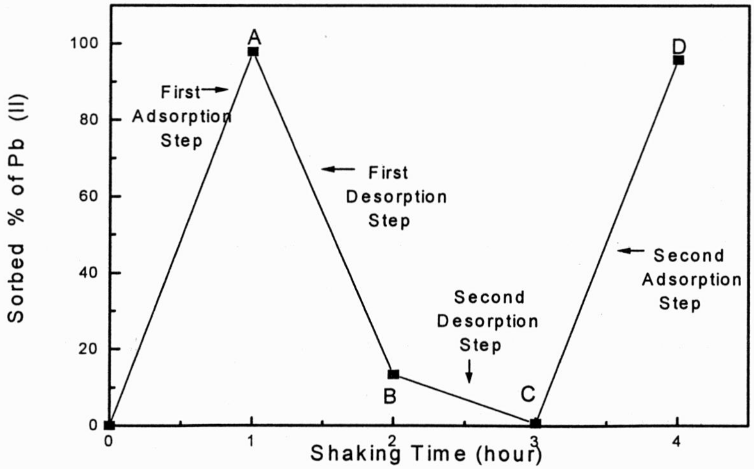

Fig. 9. A complete cycle for use and reuse of rice straw as a tester for semi-pilot application

Figure 9 shows (in percentages) sorption of Pb(II) on rice straw sample during four successive steps of adsorption and desorption. This result indicates that it is possible to decontaminate the wastes polluted with lead, even on a semi-pilot scale. This process could go through four steps, each of one hour. At point *A*, 97.9% of Pb(II) is adsorbed on RS sample after one-hour shaking at pH = 5. At point *B*, 13.4% of Pb(II) remains on RS sample after another one-hour shaking of 10^{-1} M solution of $MnCl_2$. At point *C*, 0.6% of Pb(II) remains on RS sample after another one hour shaking of 10^{-1} M solution of $MnCl_2$. At point *D*, the RS sample obtained is reused for adsorption of new Pb(II) solution. The regenerated RS sample can readsorb 95.8% of Pb(II) from a new solution at pH = 5. The whole process may proceed for four hours.

3.4. SORPTION OF Co(II)

Cobalt cations are determined in this study radiometrically. Figure 10 represents the effect of pH on adsorption of Co(II) on wheat straw sample from 0.01 M $CoCl_2$ solution. Maximum, 23.9 %, adsorption of Co(II) is reached at pH = 3.5 after 3 hour-shaking. Results of the effect of the contact time on adsorption of Co(II) from 0.01 M sulfuric acid solution on wheat straw samples at pH = 3.5 are given in figure 11. The plot shows that the highest, 25%, adsorption of Co(II) is reached after 3 hour-shaking.

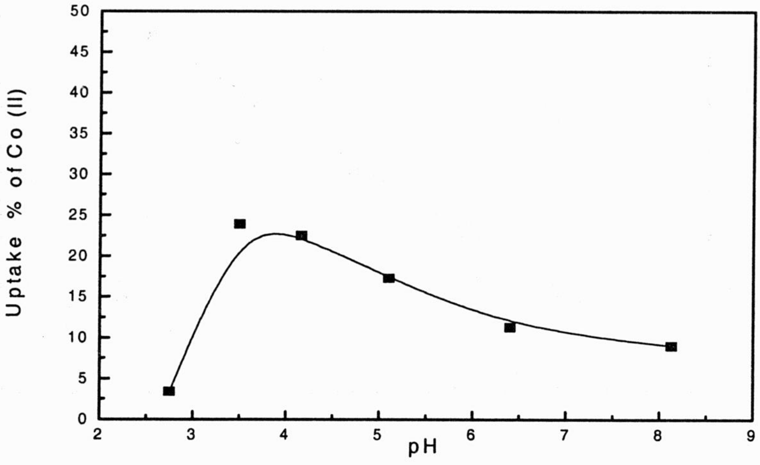

Fig. 10. Effect of pH on adsorption of Co(II) on wheat straw samples

pH equal to 3.5 has been chosen, because the effect of pH on cobalt adsorption in the experiment with straw samples was found maximal at pH = 3.5. The amounts of Co(II) adsorbed, per gram (*X*/*m*) in meq·g^{-1}, on wheat straw and sugar cane samples are plotted against Co(II) concentration in a logarithmic scale (figure 12). The plots in this figure are straight lines of the slope equal to 1. This linearity of the isotherm

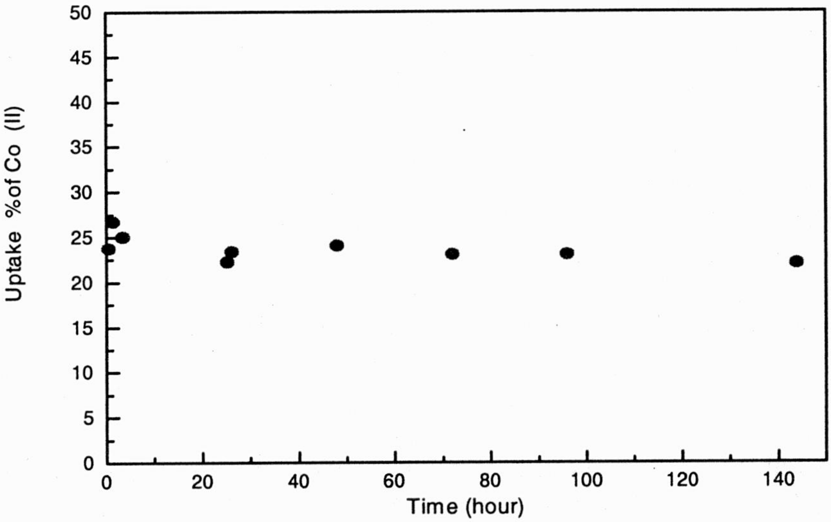

Fig. 11. Effect of contact time on adsorption of Co(II) on wheat straw samples at pH = 3.5

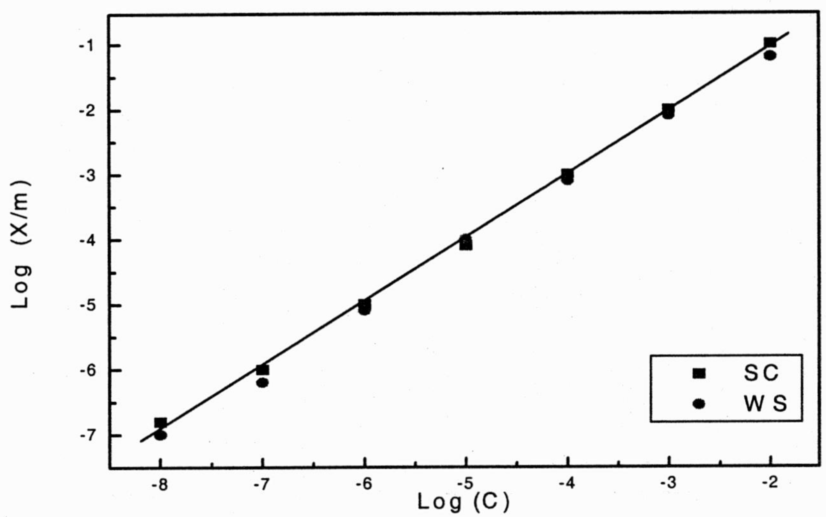

Fig. 12. Effect of ion concentration on adsorption of Co(II) on wheat straw (WS) and sugar cane residue (SC) samples

means that the adsorption process follows the Freundlich isotherm, and therefore the adsorption of Co(II) ions on straw and sugar cane residue samples takes place in result of formation of a single monolayer of ionic species being sorbed [11]. These results agree with those reported on the adsorption of various metal ions on cellulose [12] and wood powder [7], [13]. Hence, adsorption of Co(II) on maize straw follows the same mechanism as adsorption of similar metal ions on cellulose and wood powder.

3.5. DESORPTION OF Co(II)

The effect of the contact time on desorption of Co(II) from maize straw and sugar cane residue samples using distilled water is given in figure 13. Desorption of Co(II) from maize straw and sugar cane residue samples in distilled water approached ~9%. 0.1 M, 0.01 M and 0.001 M solutions of $MnCl_2$ were used as eluents for washing off Co^{2+} cations from straw and sugar cane samples (figures 14–16).

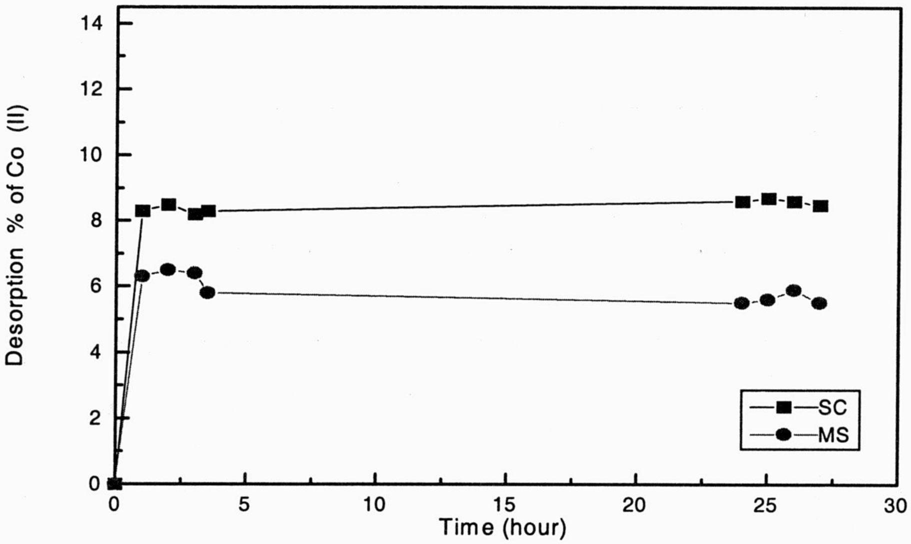

Fig. 13. Effect of contact time on desorption of Co(II) from sugar cane (SC) and maize straw (MS) samples in distilled water

Washing the Co^{2+}-loaded sugar cane samples with the solutions of 10^{-1} M $MnCl_2$ gave 27% desorption. This value decreased with the decrease in $MnCl_2$ concentration. The results of such experiments show that the percent of Co^{2+} cations eluted by distilled water is lower than the corresponding percent of Co^{2+} cations eluted by the solutions of $MnCl_2$ of different concentrations, where the Mn^{2+} cations have the similar charges and radii to the Co^{2+} cations on the sugar cane samples. So elution of the adsorbed Co^{2+} cations due to their replacement by similar cations may enhance to a certain degree the desorption process of the previously adsorbed cobalt cations which have the same charges and ionic radii as the cations used. Hence, the use of sugar cane residue in the separation processes taking place in nuclear technology is feasible.

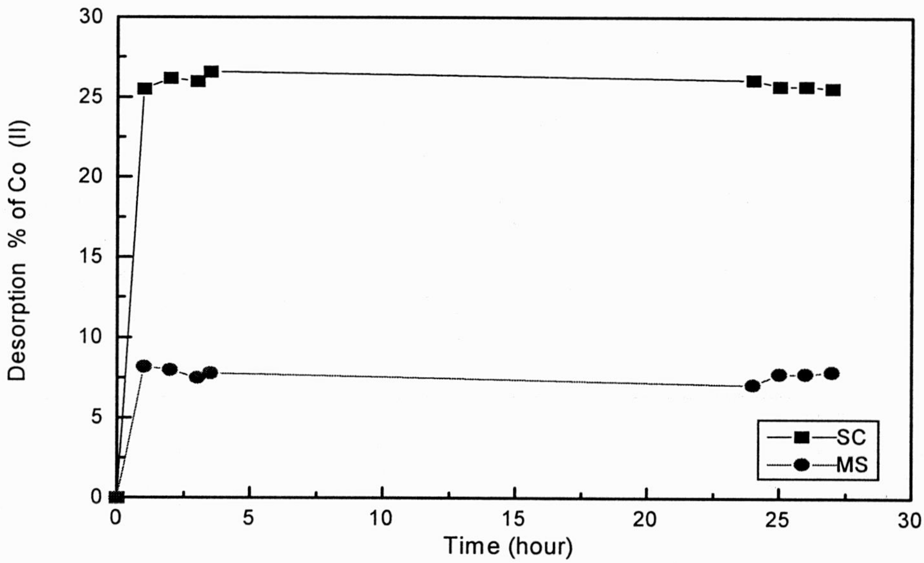

Fig. 14. Effect of contact time on desorption of Co(II) from sugar cane (SC) and maize straw (MS) samples in 0.1 M $MnCl_2$ solution

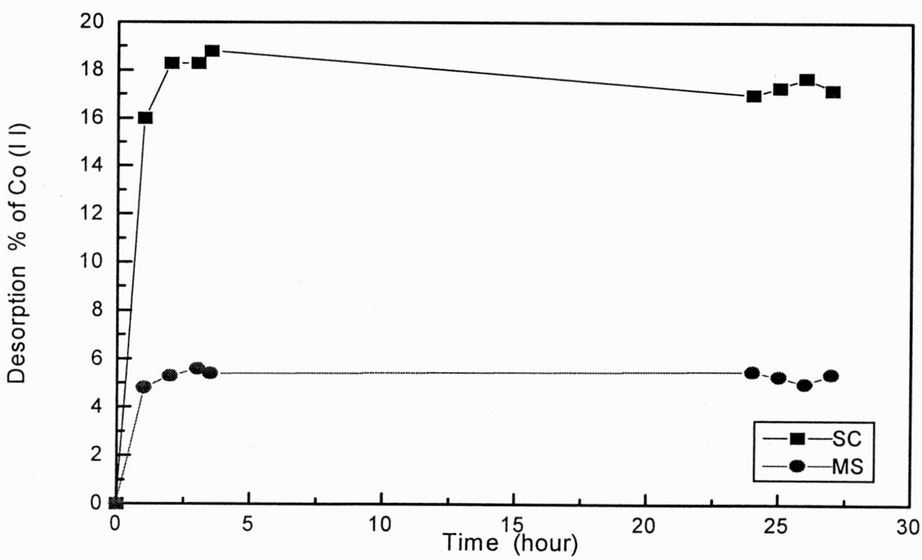

Fig. 15. Effect of contact time on desorption of Co(II) from sugar cane (SC) and maize straw (MS) samples in 0.01 M $MnCl_2$ solution

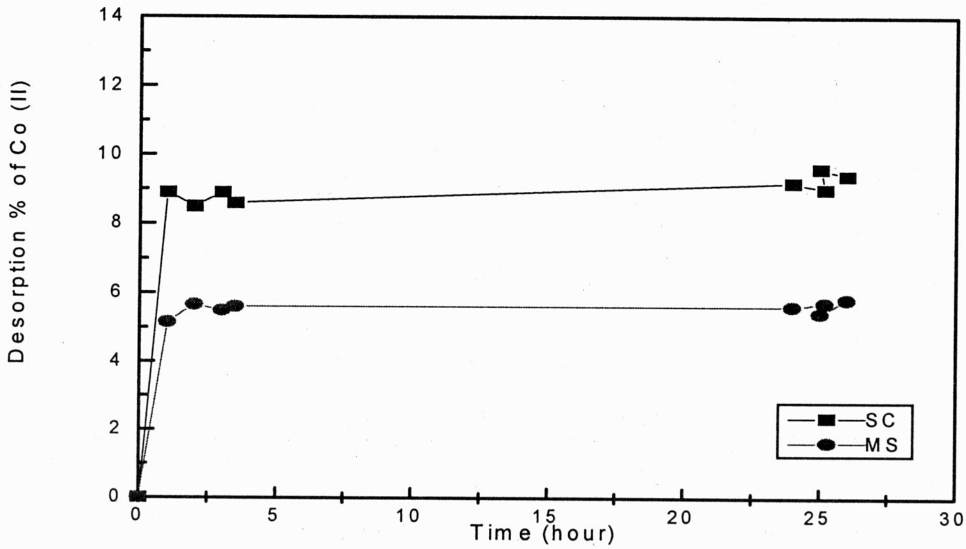

Fig. 16. Effect of contact time on desorption of Co(II) from sugar cane (SC) and maize straw (MS) samples using 0.001 M $MnCl_2$ solution

3.6. ADSORPTION OF SOME RADIONUCLIDES SUCH AS Eu(III), Co(II) AND Cs(I) FROM THEIR MIXTURE

Effect of pH variation on adsorption of Eu(III), Co(II) and Cs(I) from their mixture in diluted sulfuric acid solution has been tested (figure 17). Maximum adsorption of Eu(III) and Co(II), i.e. 49.1% and 17.2%, respectively, is reached at pH = 4. On the other hand, maximum adsorption of Cs(I) reaches 75.2% at pH = 7.2. Those results proved that the optimum pH for separating these radionuclides from their mixture under the conditions described could be 3.5. Adsorption of the three radionuclides, Eu(III), Co(II) and Cs(I), from their mixture in 0.01 M sulfuric acid solution has been studied using sugar cane, maize, wheat and rice straw samples and the results are shown in figure 18. These radionuclides were used in trace concentrations. The results of our experiment show that adsorption of Eu(III), Co(II) and Cs(I) reaches 46.46%, 21.65% and 1.4%, respectively, on rice straw sample (RS); 48.17%, 19.39% and 1.32%, respectively, on wheat straw sample (WS); 39.0%, 14.85% and 2.35%, respectively, on maize straw sample (MS); and 34.8%, 7.02% and 1.21, respectively, on sugar cane residue sample (SC).

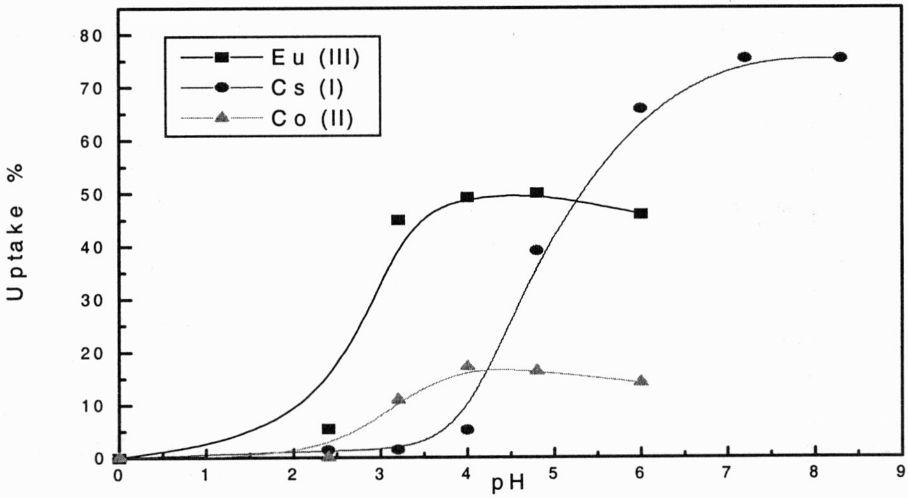

Fig. 17. Effect of pH on adsorption of Eu(III), Co(II) and Cs(I) from their mixture in sulfuric acid solution on maize straw sample

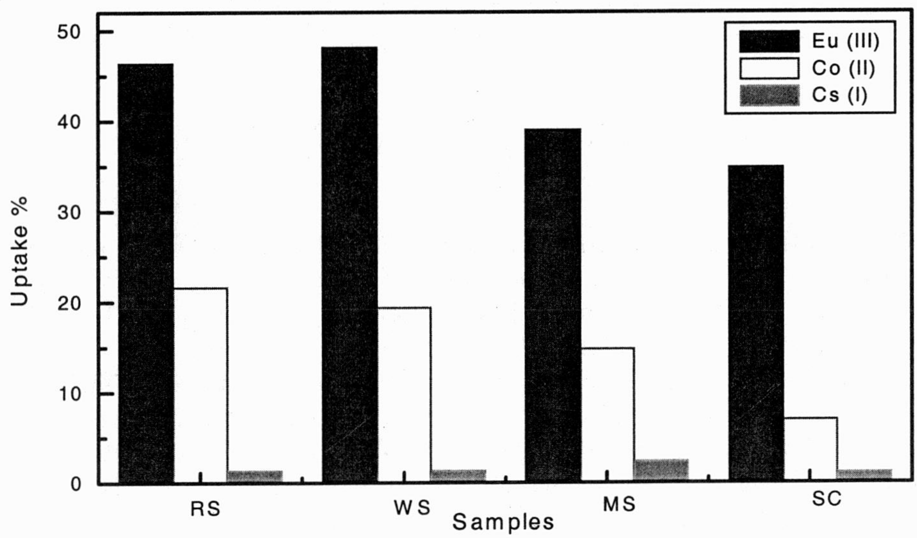

Fig. 18. Adsorption of Eu(III), Co(II) and Cs(I) from their mixture in sulfate solution of pH = 3.5 on sugar cane residue and different kinds of straw samples

On the basis of the data obtained it is clear that in 0.01 M sulfuric acid solution, europium is partially separated from cobalt and cesium at pH = 3.5 due to adsorption on straw and sugar cane samples. Various separation factors for Eu(III), Co(II) and Cs(I) are listed in table 3. Maximum values of the separation factors calculated; i.e.

Table 3

Separation factors for Eu(III), Co(II) and Cs(I) in their mixture in sulfate solution using different straw and sugar cane residue samples at pH = 3.5

Separation factor	Sugar cane (SC)	Maize straw (MS)	Wheat straw (WS)	Rice straw (RS)
$D_{Eu(III)}/D_{Co(II)}$	4.96	2.63	2.48	2.14
$D_{Eu(III)}/D_{Cs(I)}$	31.63	16.60	36.49	38.35
$D_{Co(II)}/D_{Cs(I)}$	6.38	6.32	14.69	17.89

$D_{Eu(III)}/D_{Cs(I)}$ and $D_{Co(II)}/D_{Cs(I)}$ are 38.35 and 17.89, respectively, at pH = 3.5 for rice straw sample. The separation factor for each couple of elements is obtained as the ratio of adsorption efficiency obtained for the two elements under the same conditions.

4. CONCLUSIONS

The straw samples in addition to sugar cane sample as natural, cheap materials could be used successfully for nearly complete adsorption of Pb(II) under certain experimental conditions. High sorption and desorption efficiencies of Pb(II) under certain conditions makes this method useful and feasible for environmental decontamination of waste solutions. The success of the recycling process in adsorption of Pb(II) on different straw and sugar cane residue samples may be of economic value. Successive sorption–desorption steps using these natural materials may be economic. These naturally occurring sorbents may be used successfully for partial separation of Eu(III), Co(II) and Cs(I) from their mixtures.

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USUWANIE NIEKTÓRYCH ZANIECZYSZCZEŃ ŚRODOWISKA ZA POMOCĄ NATURALNYCH MATERIAŁÓW

Opisano adsorpcję takich zanieczyszczeń jak ołów i kobalt na słomie i trzcinie cukrowej w formie odpadów poprodukcyjnych, które są przykładem naturalnych i tanich materiałów. Badano czynniki wpływające na adsorpcję wymienionych pierwiastków na różnych rodzajach słomy (ryż, pszenica, kukurydza, trzcina cukrowa). Czynniki te to: pH, czas kontaktu, stężenie jonów i typ środowiska. Podjęto próbę rozdzielenia badanych pierwiastków w ich mieszaninie. Badając adsorpcję i desorpcję ołowiu w jego środowisku przy użyciu słomy i odpadów trzciny cukrowej, zastosowano recykling. Ponowne wykorzystanie słomy i trzciny cukrowej do adsorpcji może sprawić, że będą one szeroko stosowane w półdoświadczalnych zakładach do usuwania zanieczyszczeń z odpadów. Podjęto też próbę rozdzielenia radionuklidów Eu(III), Cd(II) i Cs(I) w ich mieszaninie. Zastosowano radiometryczne i spektrofotometryczne techniki analityczne.