

## In-Situ Immobilization Remediation of Soils Polluted with Lead, Cadmium and Nickel

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**Abstract:** In-Situ immobilization technique was used for remediation of lead, cadmium and nickel polluted soils. Two rates (0.5 and 1%) of five immobilizing agents (bentonite, barite, kaolinite, dowex and silica-gel) were tested on soils containing various levels of available Pb (24-77.3 mg kg<sup>-1</sup>), Cd (0.98-2.6 mg kg<sup>-1</sup>) and Ni (19.3-45.7 mg kg<sup>-1</sup>). Incubation experiment was conducted to study the effect of these agents on soil available content of Pb, Cd and Ni. All the tested immobilizing agents decreased the soil available Pb, Cd and Ni extracted by DTPA. The ability of these agents in immobilizing Pb, Cd and Ni increased with increasing their rate of application and could be arranged in descending order as follows: dowex > silica-gel > bentonite > barite > kaolinite. Dowex showed the highest ability to immobilize heavy metals in soils. It decreased DTPA extractable Pb, Cd and Ni by 89.5-95.7 %, 74.6-90.8 % and 80.2-88.9 % of the initial, respectively. Kaolinite showed the lowest ability to immobilize these metals in soils, as it decreased available Pb, Cd and Ni by 35.4-63.5 %, 43-52 % and 43.7-56.5 %, respectively. Lead, cadmium and nickel fractionations were performed using a sequential chemical extraction. Dowex and bentonite clays decreased the exchangeable form of Pb, Cd and Ni in all the studied soil samples. Carbonate, oxide, organic and residual forms were rarely affected, with all the studied soil samples.

**Key words:** Immobilization • Contamination • Remediation • Lead • Nickel • Cadmium • Fractions

### INTRODUCTION

Heavy metals pollution is responsible for several environmental problems and risks to human health, including decrease soil microbial activity, fertility and yield losses. Actually, large areas of land are contaminated with heavy metals deriving from urban activities (municipal sewage sludge and other waste incinerators); agricultural operations (fertilizers and pesticides application) and industrial processing (smelting industry, paint factory and tannery). Consequently, the use of plants contaminated with high levels of heavy metals for food, might pose a serious risk to human and animal health [1].

Usually remediation methods applicable to soils contaminated with heavy metals are based on two approaches: removal/extraction of the heavy metals from soil matrix by electro kinetic and/or washing processes which are characterized by high costs and laborious management [2, 3] or reduction of metal mobility with in situ techniques.

In-Situ immobilization techniques using the addition of chemicals to contaminated soil were used to reduce the solubility of metals through metal sorption or and/or precipitation and thus; reducing metal transport from

contaminated soil to surface and ground water [4]. According to Basta and Sloan [5], in situ immobilization of heavy metals by amendment of immobilizing reagents is the only option to avoid the potential availability of heavy metals to living beings, although heavy metals remain in soils in this process [6].

Silica gel has been adopted as a good alternating support for chelating heavy metals. This is due to its specific surface area and silanol group [7, 8]. Many types of chelate resins and ion-exchange resins such as Dowex were used for immobilize metals because it has surface functional groups [9]. The high specific surface area, chemical stability, layered structure, high cation-exchange capacity, etc., have made the bentonite clays excellent adsorbent materials [10]. The application of Barite (BaSO<sub>4</sub>) is seen as a favorable way to in-situ immobilizing heavy metals within porous rock or soil formations. Due to the extremely low solubility of barite a long time stable immobilization is achieved [11].

This study was undertaken to evaluate the efficiency of various amendments of bentonite, silica-gel, kaolinite, dowex and barite, to stabilize Pb, Cd and Ni in some polluted soils to unavailable forms. The effect of the studied agents on metal fractions was also tested.

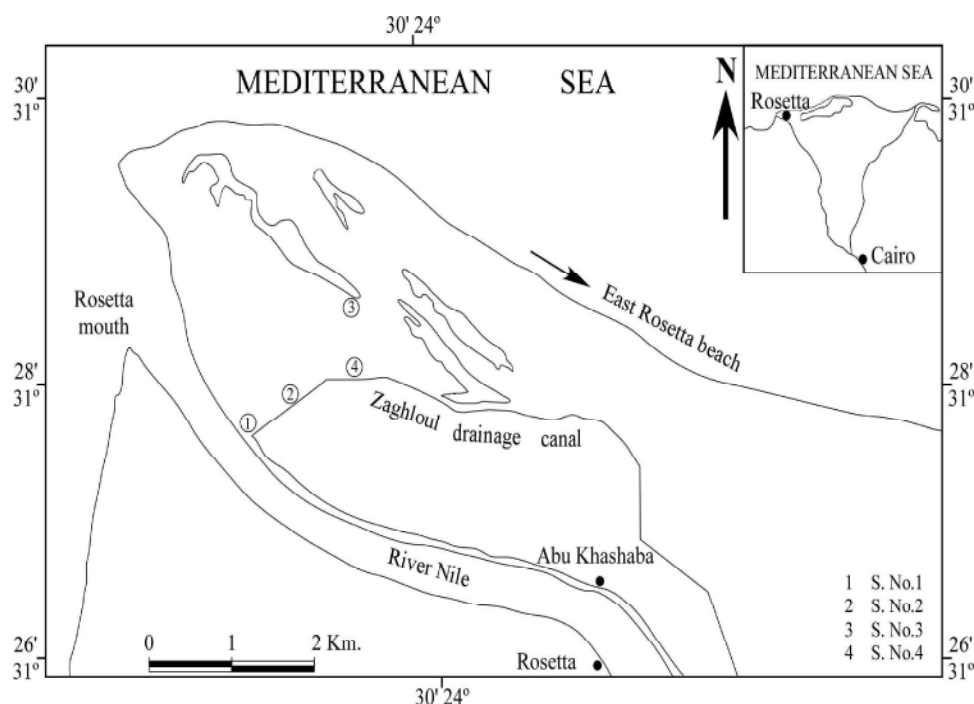


Fig. 1: Location of the studied area and the studied soil samples

## MATERIALS AND METHODS

The studied area lies between longitudes 30° 22'-30° 26' East and latitudes 31° 26'-31° 30' North (Fig. 1). Four surface soil samples (0-25 cm) were collected from East Rosetta Estuary, Egypt. These soils are contaminated by heavy metals from domestic, industrial wastes and sewage sludge.

The collected soil samples were air dried and sieved to pass through a 2mm sieve. Soil particles size distribution was performed according to the pipette method [12]. Organic matter content was determined according to the modified Walkley and Black method and total carbonates were determined gasometrically by using collins calcimeter and calculated as  $\text{CaCO}_3$  [13].

Soil pH and electrical conductivity were determined using glass electrode in a soil to water

suspension ratio of 1:2.5 [13]. Cation exchange capacity (CEC) was determined by Na-acetate at pH 7 [14]. The general characteristics of the studied soil samples are shown in Table 1.

Available Pb, Cd and Ni were extracted using DTPA [15]. Total concentration of the metals was extracted by fusion with mixture of concentrated acids [16]. Pb, Cd and Ni were determined using (AAS) atomic absorption spectrophotometer (GBC-932). The available and total concentrations of Pb, Cd and Ni in soils are presented in Table 2.

Sequential extraction of heavy metals was carried out according to Tessier *et al.* [17]. Lead, cadmium and nickel were partitioned into five operationally defined fractions, i.e., exchangeable, bound to carbonates, reducible (bound to Fe- Mn oxides), oxidizable (bound to organic matter and/or sulfides) and residual.

Table 1: The general characteristics of the studied soil samples

S.No.	pH 1:2.5	EC 1:2.5 dSm <sup>-1</sup>	CaCO <sub>3</sub> %	CEC Cmol k <sup>-1</sup>	O.M. %	Particle size distribution			Texture
						Sand %	Silt %	Clay %	
1	8.07	1.26	0.83	22.70	0.89	47.0	25.0	28.0	Sandy clay loam
2	7.53	2.10	1.14	17.56	0.80	62.5	17.5	20.0	Sandy loam
3	7.94	2.60	1.45	4.69	0.54	89.0	5.5	5.5	Loamy sand
4	7.40	0.67	1.86	3.88	0.61	92.0	4.5	3.5	Sand

Table 2: The total and available contents of heavy metals in the studied soils

S.N	Total content (mg/kg)			DTPA extractable (mg/kg)		
	Pb	Cd	Ni	Pb	Cd	Ni
1	289	10	55	24.0	2.6	19.3
2	244	5	305	35.9	1.0	37.7
3	157	20	212	47.2	2.1	45.7
4	380	5	75	77.3	1.0	21.0

Five immobilizing agents were tested in the present study. The tested agents were:

- Silica gel: obtained from El-Gomhoriya Company for chemicals.
- Kaolinite: clay mineral obtained from sedimentary rocks at Kalabsha area, Aswan.
- Dowex 50W, X12: cation exchange resin produced by BDH chemical Ltd Poole, England, standard grade.
- Bentonite: clay mineral obtained from central Eastern desert.
- Barite mineral ( $\text{BaSO}_4$ ): obtained from sedimentary rocks at Bahariya oasis.

An incubation experiment was performed to assess the influence of the tested agents to stabilize Pb, Cd and Ni in the tested soils. The soil samples were treated with the five amendments individually at two rates of 0.5 and 1.0 %. Two 20g portions of each soil were transferred to 100 ml glass bottle. Each bottle received 20 ml of deionized water containing the appropriate amount of the immobilizing agent. The treated soils were then dried in an oven, at 40°C for 3.5 days. The soil was subjected to four alternatively wet (with 10 ml of deionized water) and dry cycles (28 days). At the end of incubation time the soils

were crushed to pass through a 2mm sieve and analyzed for DTPA extractable and also for various fractions of Pb, Cd and Ni.

## RESULTS AND DISCUSSION

**Stabilization of Heavy Metals in Soils:** The data presented in Table 3 and Fig. 2 shows that all the tested agents reduced the mobile pool of Pb of the treated soils. However, the magnitude of reduction varied widely according to the type of immobilizing agent and rate of its addition. In general, for all soils and all tested agents, DTPA extractable Pb decreased as the rate of immobilizing agent increased. DTPA extractable Pb decreased by values ranged between 26.3-70.5 % of the untreated soil when soils treated with agents at rate of 0.5%. On the other hand, the application rate of 1% was rather effective in reducing DTPA extractable by values ranged between 35.4-95.7 % of the untreated soil.

Dowex treatment is the most effective immobilizing agents. The results indicated that the application of dowex at rate of 1 % was more efficiency in decreasing DTPA extractable Pb by values ranged between 89.5-95.7 % as compared to untreated one. The percent decreases in DTPA extractable Pb was 69.3-88.3, 53.4-80.2,

Table 3: DTPA extractable-Pb ( $\text{mg kg}^{-1}$ ) of the studied soil samples before and after treating the soils with two rates of five immobilizing agents

Treatments	Rate of addition (%)	DTPA-extractable Pb ( $\mu\text{g/g}$ ) in soil			
		Soil 1	Soil 2	Soil 3	Soil 4
Initial	0.0	24.00	35.87	47.23	77.34
Silica-gel	0.5	9.41	13.38	20.59	35.89
	1.0	2.81	6.38	9.40	23.74
Bentonite	0.5	11.04	15.60	24.28	41.53
	1.0	4.75	8.36	12.52	36.04
Dowex	0.5	7.60	10.55	16.74	24.97
	1.0	1.50	3.34	2.03	8.12
Kaolinite	0.5	14.82	23.57	33.86	57.00
	1.0	8.76	17.22	27.58	49.96
Barite	0.5	12.46	20.77	30.89	53.21
	1.0	6.14	14.06	19.75	42.69

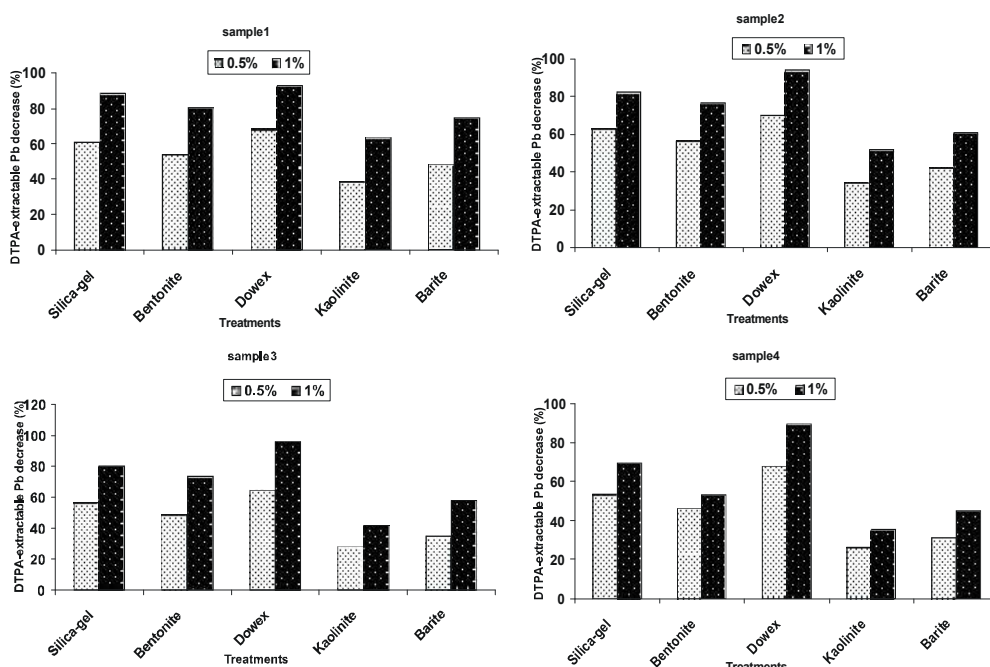


Fig. 2: Effect of various immobilizing agents on DTPA extractable- Pb decrease (%) as compared with untreated soils

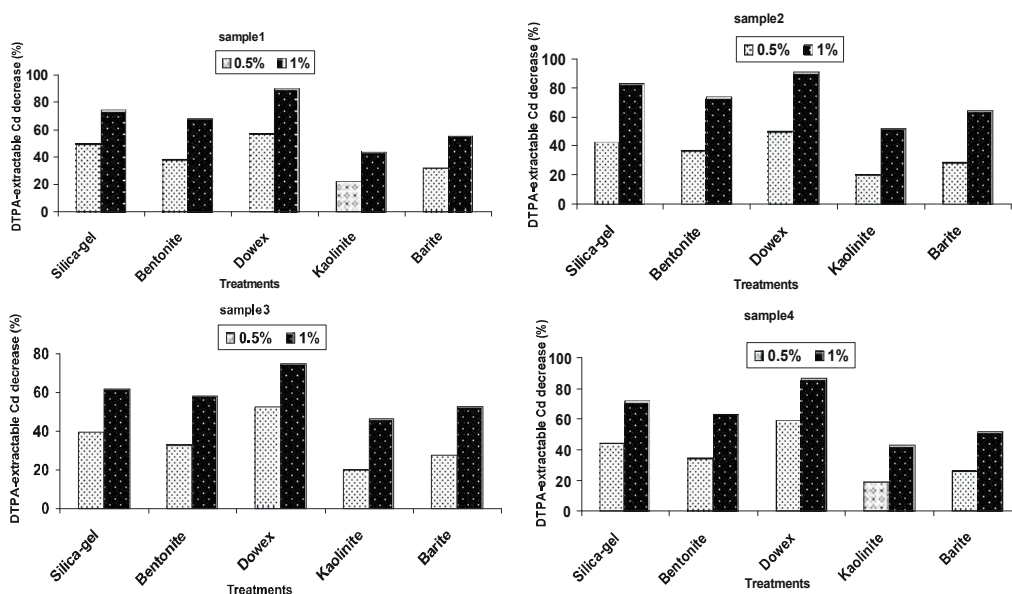


Fig. 3: Effect of various immobilizing agents on DTPA extractable-Cd decrease (%) as compared with untreated soils

44.8-74.4 and 35.4-63.5 % when adding 1% of silica gel, bentonite, barite and kaolinite, as compared to untreated soils, respectively.

Based on the obtained results, the tested agents could be arranged according to their efficiency in immobilizing Pb from the studied soils in descending order as follows: dowex > silica-gel > bentonite > barite > kaolinite.

Although the studied soils contain low levels of DTPA extractable Cd compared with those of Pb, the effect of different immobilizing agents on the stabilizing mobile pool of Cd in the studied soils was almost similar to that on Pb.

The results presented in Table 4 and Fig. 3 show that the efficiency of various agents in stabilizing Cd increased as their application rates increased. Treating the soils with

Table 4: DTPA extractable-Cd ( $\text{mg kg}^{-1}$ ) of the soil samples before and after treating the soils with two rates of five immobilizing agents

Treatments	Rate of addition (%)	DTPA-extractable Cd ( $\mu\text{g/g}$ ) in soil			
		Soil 1	Soil 2	Soil 3	Soil 4
Initial	0.0	2.57	0.98	2.09	1.00
Silica-gel	0.5	1.30	0.56	1.27	0.56
	1.0	0.66	0.17	0.80	0.28
Bentonite	0.5	1.58	0.62	1.41	0.65
	1.0	0.83	0.26	0.87	0.37
Dowex	0.5	1.12	0.49	1.00	0.41
	1.0	0.26	0.09	0.53	0.13
Kaolinite	0.5	2.00	0.78	1.67	0.81
	1.0	1.45	0.47	1.12	0.57
Barite	0.5	1.76	0.70	1.52	0.74
	1.0	1.14	0.35	0.99	0.48

Table 5: DTPA extractable-Ni ( $\text{mg kg}^{-1}$ ) of the soil samples before and after treating the soils with two rates of five immobilizing agents

Treatments	Rate of addition (%)	DTPA-extractable Ni ( $\mu\text{g/g}$ ) in soil			
		Soil 1	Soil 2	Soil 3	Soil 4
Initial	0.0	19.31	37.69	45.70	21.00
Silica-gel	0.5	13.32	25.44	32.26	14.11
	1.0	5.00	9.95	12.61	5.40
Bentonite	0.5	15.04	26.99	35.46	15.60
	1.0	6.24	13.42	14.40	7.67
Dowex	0.5	10.18	18.58	23.63	10.58
	1.0	3.82	5.43	5.07	2.88
Kaolinite	0.5	16.28	30.53	37.61	17.45
	1.0	8.40	18.69	23.49	11.82
Barite	0.5	11.64	22.92	29.93	12.47
	1.0	7.86	16.21	21.80	10.10

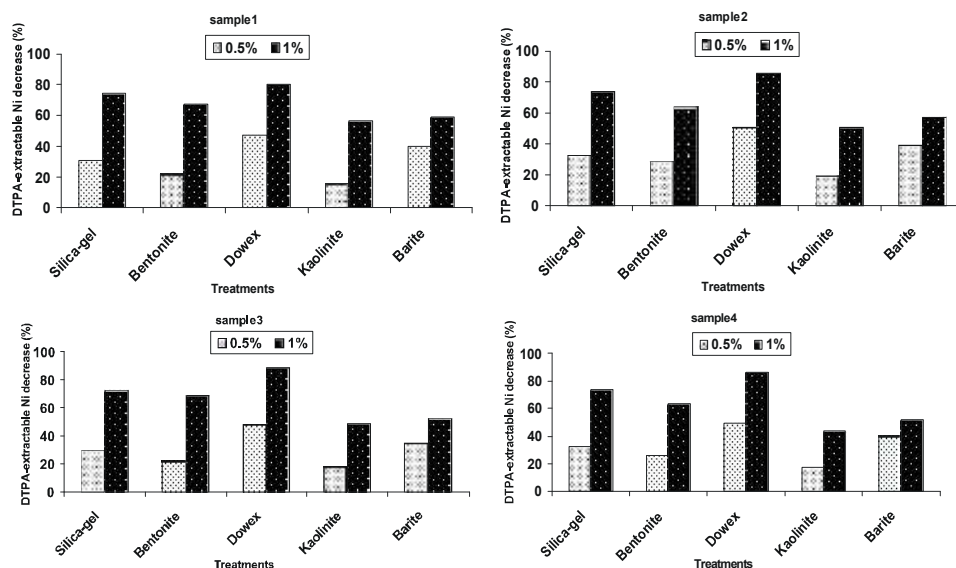


Fig. 4: Effect of various immobilizing agents on DTPA extractable-Ni decrease (%) as compared with untreated soils

rates of 0.5 %, decreased DTPA extractable Cd by values ranged between 19-59 %, compared to untreated soils. The corresponding values at the application rate of 1% ranged between 43-90.8 % compared to untreated soils.

The percent decreases in DTPA extractable Cd were 74.6-90.8, 61.7-82.6, 58.4-73.5, 52-64.3 and 43-52 % for dowex, silica-gel, bentonite, barite and kaolinite, respectively.

From the results listed in Table 5 and presented in Fig. 4, the application rates of 0.5% were much less effective in reducing DTPA extractable Ni by values ranged between 15.7-50.7 % while the application rates of 1 % decreased DTPA extractable Ni by values ranged between 43.7 and 88.9 % compared to untreated soils.

The obtained results of adding 1 % agent decreased the DTPA extractable-Ni by 80.2-88.9, 72.4-74.3, 63.5-68.5, 51.9-59.3 and 43.7-56.5 % compared to untreated soils for dowex, silica-gel, bentonite, barite and kaolinite, respectively.

#### Distribution of Pb, Cd and Ni in Soil Fractions:

The behavior of heavy metals in soils depends not only on the level of contamination as expressed by the total content, but also on the form of the metal. Fractionation of heavy metals provides a useful tool to understand the chemistry of these metals in soils. The distribution of heavy metals among the different soil chemical fractions was determined before and after treating the soil samples with the tested immobilizing agents at the application rate of 1% (Tables 6- 8).

The employed procedure succeeded in recovering amounts almost closed to the total amounts of the different elements. A high significant correlation coefficient value was found between the total metals in soils and sum of the different metal fractions 0.999, 0.998 and 0.999 for Pb, Cd and Ni, respectively.

Pb was mainly found in the residual fraction. It constitutes 48 % of the sum of Pb fractions, followed by organic fraction (17%), carbonate (15 %) and oxide (11%). Exchangeable fraction constitutes the least ( 9 %) of the sum of Pb fractions. Almost the same trend was found for Cd and Ni, except that oxide fraction is more than carbonate fraction for Cd and more than organic fraction followed by carbonate fraction for Ni. Cd in the Res., Org., Oxide, Carb. and Exch. fractions represents 31, 20, 18, 16 and 15 % of the sum of Cd fractions, respectively. For Ni, the Res. fraction constitutes 39 % of the sum of Ni fractions, followed by oxide (18 %), Org. (17 %), Carb. (13%) and Exch. fraction constitutes the least (12 %) of the sum of Ni fractions.

The distribution of metals fractions was in the order: Res.> Org.> Carb.> oxide > Exch. for Pb, Res.> Org.> oxide.> Carb. > Exch. for Cd and Res.> oxide.> Org.> Carb. > Exch. for Ni.

Table 6: Different fractions of Pb ( $\text{mg kg}^{-1}$ ) sequentially extracted from the tested soils before and after incubation and treating with immobilizing agents

		Pb fractions ( $\text{mg.kg}^{-1}$ )					
S.N		Ex.	Carb.	Oxide.	Org.	Res.	Sum
Initial	Soil 1	8.4	26.0	18.6	61.3	160.1	274.4
	Soil 2	18.1	40.0	22.3	56.1	90.0	226.5
	Soil 3	25.6	23.0	19.3	8.8	69.0	145.7
	Soil 4	28.1	59.0	48.3	46.1	170.0	351.5
Silica-gel	Soil 1	8.2	25.8	18.6	61.2	160.1	273.9
	Soil 2	18.2	39.1	22.3	56.0	90.0	225.6
	Soil 3	24.9	24.1	19.3	8.7	69.0	146.0
	Soil 4	27.8	58.6	48.3	46.0	170.0	350.7
Bentonite	Soil 1	5.1	26.5	18.5	61.8	160.0	271.9
	Soil 2	10.7	40.7	22.1	56.9	89.6	220.0
	Soil 3	12.1	24.9	19.2	16.7	68.8	141.7
	Soil 4	17.5	60.5	48.1	51.6	167.0	344.7
Dowex	Soil 1	4.9	26.4	18.3	62.8	160.0	272.4
	Soil 2	9.8	40.6	22.2	57.9	89.9	220.4
	Soil 3	11.4	25.5	19.1	10.9	68.9	135.8
	Soil 4	16.3	60.5	48.2	53.2	168.1	346.3
Kaolinite	Soil 1	8.3	26.2	18.7	61.4	159.0	273.6
	Soil 2	18.0	40.2	22.5	56.3	89.0	226.0
	Soil 3	25.3	23.1	19.4	8.9	68.7	145.4
	Soil 4	28.0	59.5	48.6	47.0	168.0	351.1
Barite	Soil 1	8.2	26.1	18.8	61.4	159.1	273.6
	Soil 2	18.1	40.1	22.4	56.2	89.8	226.6
	Soil 3	25.5	22.4	19.5	9.1	68.8	145.3
	Soil 4	27.9	59.5	49.1	46.7	166.0	349.2

Table 7: Different fractions of Cd (mg kg<sup>-1</sup>) sequentially extracted from the tested soils before and after incubation and treating with immobilizing agents

		Cd fractions (mg.kg <sup>-1</sup> )					
S.N		Ex.	Carb.	Oxide.	Org.	Res.	Sum
Initial	Soil 1	1.1	1.3	1.5	2.6	3.3	9.8
	Soil 2	1.0	1.0	0.8	0.5	1.4	4.7
	Soil 3	1.8	2.2	3.6	4.3	6.2	18.1
	Soil 4	0.8	0.8	0.9	0.9	1.2	4.6
Silica-gel	Soil 1	0.8	1.2	1.5	2.5	3.3	9.3
	Soil 2	0.7	0.9	0.8	0.4	1.4	4.2
	Soil 3	1.5	2.1	3.6	4.2	6.2	17.6
	Soil 4	0.5	0.7	0.9	0.8	1.2	4.1
Bentonite	Soil 1	0.4	1.9	1.3	3.1	2.8	9.5
	Soil 2	0.4	1.3	0.6	0.8	1.3	4.4
	Soil 3	0.6	2.5	3.5	5.2	5.9	17.7
	Soil 4	0.3	1.5	0.7	1.2	0.8	4.5
Dowex	Soil 1	0.3	1.7	1.4	3.2	3.0	9.6
	Soil 2	0.3	1.2	0.7	0.9	1.0	4.1
	Soil 3	0.5	2.6	3.4	5.6	5.8	17.9
	Soil 4	0.2	1.4	0.8	1.3	0.7	4.4
Kaolinite	Soil 1	1.0	1.4	1.6	2.7	3.1	9.8
	Soil 2	0.9	1.1	0.9	0.6	1.1	4.6
	Soil 3	1.7	2.3	3.7	4.1	6.0	17.8
	Soil 4	0.6	0.9	1.0	1.0	1.1	4.6
Barite	Soil 1	0.9	1.6	1.7	2.1	3.1	9.4
	Soil 2	0.8	1.1	1.0	0.6	1.2	4.7
	Soil 3	1.6	2.3	3.8	4.2	6.1	18.0
	Soil 4	0.7	1.0	1.0	1.1	0.7	4.5

Table 8: Different fractions of Ni (mg kg<sup>-1</sup>) sequentially extracted from the tested soils before and after incubation and treating with immobilizing agents

		Ni fractions ( mg.kg <sup>-1</sup> )					
S.N		Ex.	Carb.	Oxide.	Org.	Res.	Sum
Initial	Soil 1	4.7	6.7	10.6	9.6	20.1	51.7
	Soil 2	33.0	48.0	63.0	35.4	121.4	300.3
	Soil 3	24.0	30.0	40.5	29.0	74.5	197.7
	Soil 4	12.5	7.0	8.30	16.5	27.0	71.3
Silica-gel	Soil 1	3.9	6.6	10.6	9.5	20.1	50.7
	Soil 2	30.0	46.0	63.0	35.1	121.4	295.5
	Soil 3	20.7	31.7	40.5	28.5	74.1	195.5
	Soil 4	11.5	6.9	8.30	16.3	26.4	69.4
Bentonite	Soil 1	2.7	7.1	10.4	10.0	19.8	50.0
	Soil 2	17.6	50.4	62.9	44.9	121.3	297.1
	Soil 3	12.4	31.5	40.1	33.8	74.3	192.1
	Soil 4	8.2	7.8	8.10	20.0	26.5	70.6
Dowex	Soil 1	2.6	7.2	10.5	9.9	19.7	49.9
	Soil 2	15.8	50.6	62.7	45.8	121.1	296.0
	Soil 3	10.7	31.9	40.2	35.9	74.4	193.1
	Soil 4	7.1	7.9	8.20	21.1	26.8	71.1
Kaolinite	Soil 1	4.6	6.8	10.8	9.7	19.7	51.6
	Soil 2	32.0	48.3	63.3	35.5	121.2	300.3
	Soil 3	22.5	30.6	41.0	29.7	73.8	197.6
	Soil 4	12.1	7.3	8.50	16.1	26.2	70.2
Barite	Soil 1	4.5	6.9	10.7	9.7	19.9	51.7
	Soil 2	31.0	48.7	63.4	35.5	121.2	299.8
	Soil 3	21.5	30.7	41.2	29.4	73.9	196.7
	Soil 4	12.3	7.4	8.40	16.0	26.3	70.4

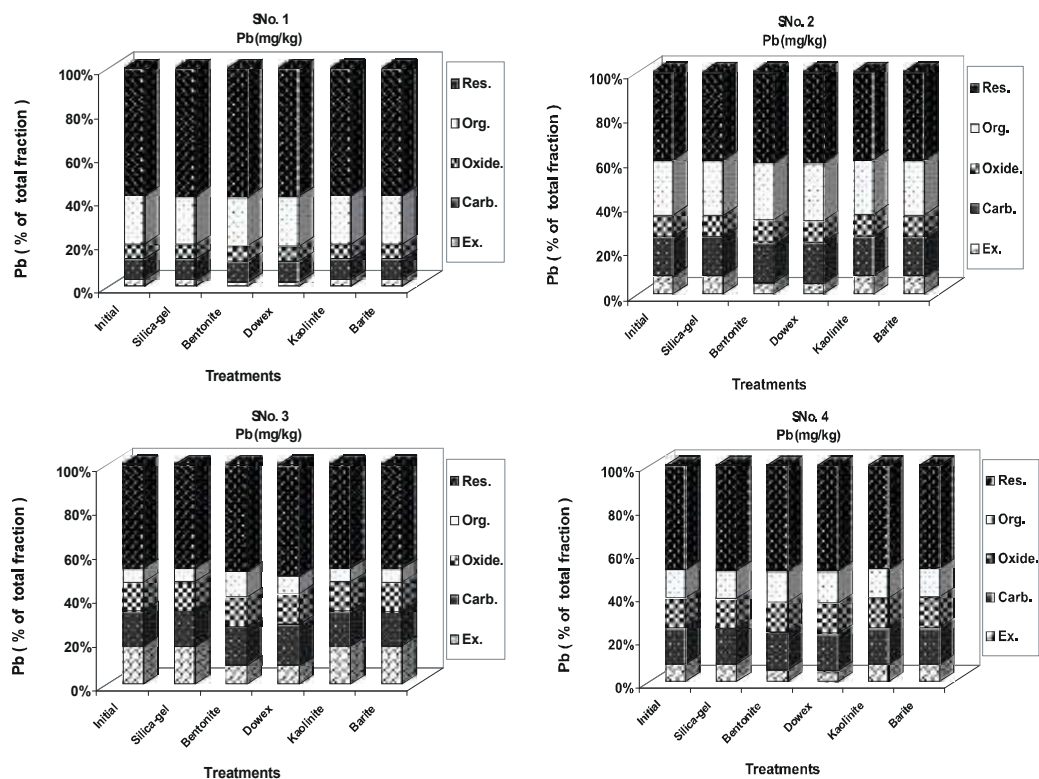


Fig. 5: Effect of immobilizing agents on distribution of Pb among different chemical fractions

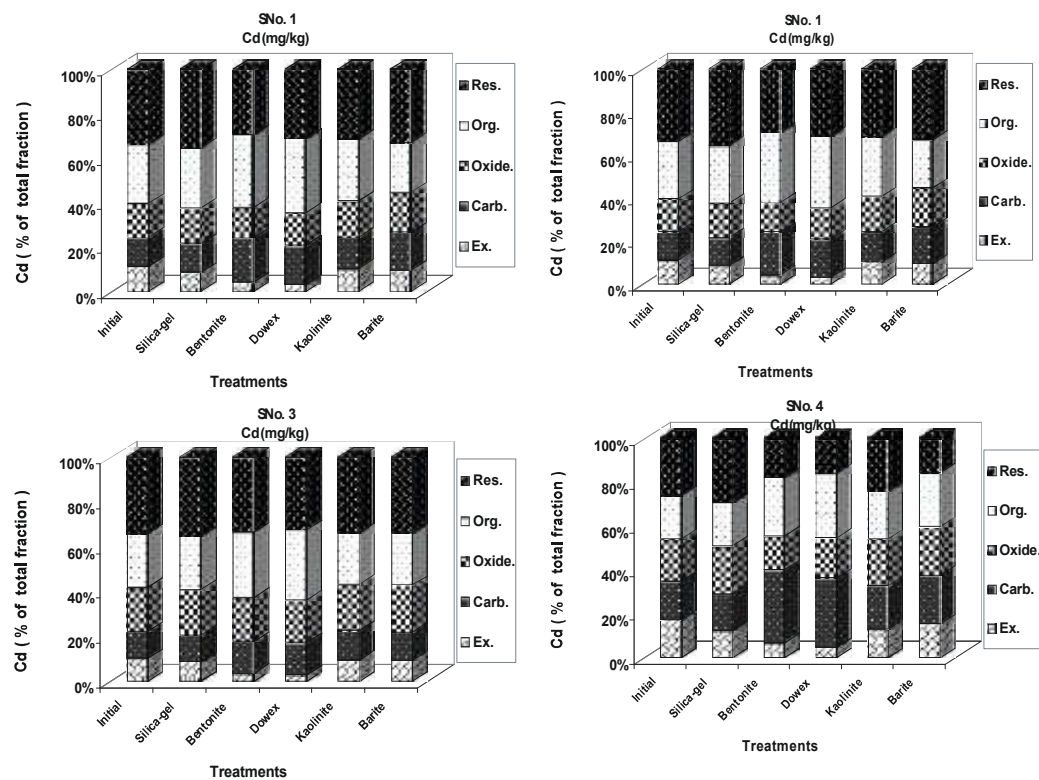


Fig. 6: Effect of immobilizing agents on distribution of Cd among different chemical fractions



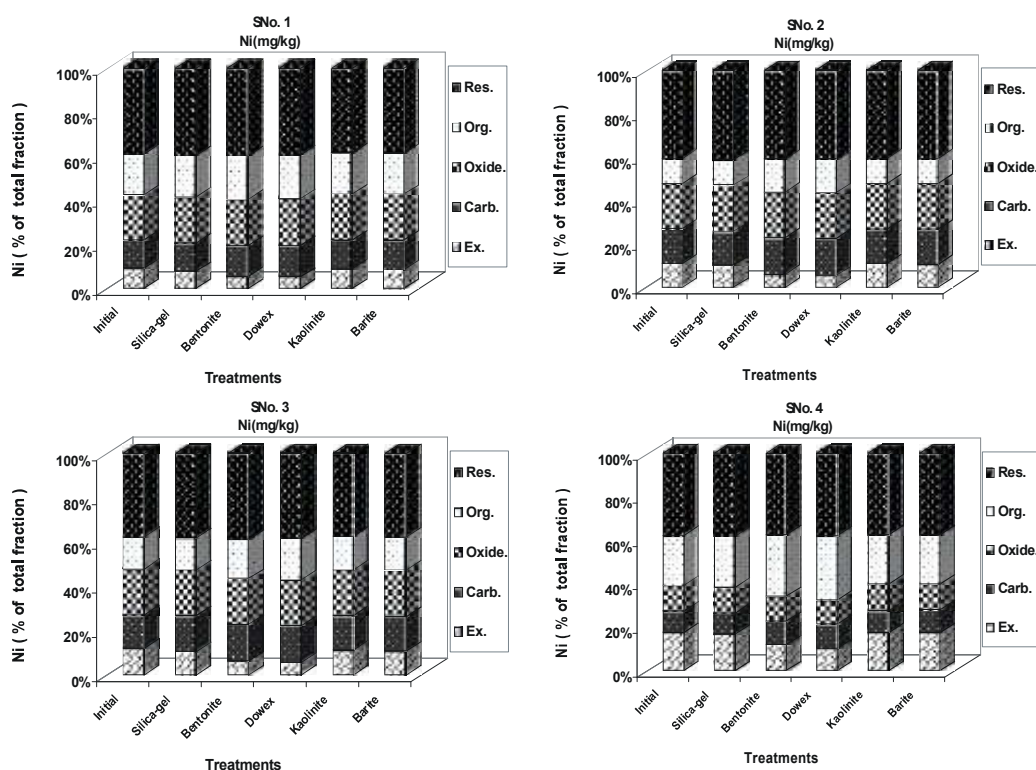


Fig. 7: Effect of immobilizing agents on distribution of Ni among different chemical fractions

Dowex and bentonite clays (Figs. 5-7) caused a considerable decrease in Exch. fraction (the most mobile fraction) of Pb, Cd and Ni in all the studied soil samples. Carb., Oxide, Org. and Res. fractions seemed to be not affected with all the tested agents.

Dowex decreased Exch. fraction for all the studied soil metals in all the studied soil samples by 45-58, 25-30 and 45-57 % less than the initial Pb, Cd and Ni, respectively. Based on the chemical composition of dowex as cation exchanger (styrene divinyl benzene copolymers), the most accepted process in fixing mobile Pb is complexation and/or with the selectivity of sulfonic acid group ( $\text{SO}_3\text{H}$ ) of the resin [18].

Marked decrease was obtained for Exch. fraction for all the studied soil metals upon treating soil samples with bentonite clays by 47-62, 33-40 and 52-66 % less than the initial for Pb, Cd and Ni, respectively. Bentonite clays have high specific surface area, chemical and mechanical stability, layered structure, high cation-exchange capacity that made the clays excellent adsorbent material.

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