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Immobilization of chromium and other metals in contaminated sediments from Northern Morocco ports using mineral additives

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Abstract

The fate of dredged sediments is a major problem in some countries due to significant contamination organic and mineral pollutants. Land disposal dredged sediment must be accompanied treatment to limit the dispersion of pollutants in the environment.

In this paper,laboratory batch adsorption experiments were used at room temperature (25 °C) to evaluate the feasibility of using low cost mineral additives as stabilization agents of heavy metals, especially chromium, from dredged sediments. Our results indicate that the adsorption of Cr(VI) depends strongly on the pH (2-11), but is independent of ionic strength (0.01, 0.05 and 0.1 M) for Hematite. For Kaolinite, adsorption is strongly dependent on pH values (2-11) and ionic strength (0.01, 0.05 and 0.1 M). Then,batch leaching methods were used to evaluate the effectiveness of hematite and kaolinite, as additives for reducing the mobilization of heavy metals, especially chromium, from contaminated dredged sediments. The obtained results demonstrate that the addition of amendments could be a successful technique for stabilization of chromium and other metals in contaminated sediment.

Keywords: Stabilization; Hexavalent Chromium; Sediment; Mineral Additives; Adsorption

1. Introduction

Because of their natural properties, sediments can accumulate hazardous heavy metals, known for their significant toxicity for humans, animals, microorganisms and plants. The potential risk of heavy metals in sediments, with respect to their mobility and eco-toxicological significance, is determined by their solid-solution partitioning rather than the total heavy metal content, if they are readily released into sediment solution or are otherwise available to biological processes [1-3]. The release of heavy metals to the water phase (leaching) and so the susceptibility for transport processes depends on their solution speciation and their affinity to bind to reactive surfaces in the sediment matrix. However, if such metals are bound up in relatively inert and insoluble compounds, the danger they represent is reduced substantially.

Morocco is presently experiencing a great deal of economic development, which often brings about the risk of pollution by toxic chemicals. That is why it is imperative to reconcile economic development with the quality of the environment. The sediments dredged are indeed often polluted with heavy metals and organic matter and may present a risk for the environment and human health [4]. It is therefore necessary to propose appropriate treatment techniques that satisfy environmental as well as economic criteria.

In Morocco, approximately 4Mm^3 of the sediments are dredged each year. Dredged sediments are frequently accumulating chemicals and present an effective contamination risk for coastal waters, affecting the ecosystems durably. In sediment, chromium behaviour is governed by pH, Eh and organic matter [5-8]. Its adsorption by clay and Fe or Al (oxy)hydroxides is also highly dependent on pH; Cr(VI) adsorption decreases with increasing pH [9], and Cr(III) adsorption increases with increasing pH [10, 11]. Trivalent chromium has low solubility and mobility in aqueous medium at alkaline and neutral pH [12]. Thus, its toxicity for mammals and aquatic organisms is low in comparison with other metals [13]. However, it is fundamental in low amounts as essential nutrient for maintaining the metabolism of glucose and an appropriate function of insulin hormone [14]. Hexavalent chromium, one of the extremely toxic heavy metals, can cause health problemssuch as liver damage, pulmonary congestions, vomiting, and severe diarrhea [15, 16].

Chromium in sediments may be presented in one of two thermodynamically stable oxidation states: Cr(III) or Cr(VI) [17]. The Oxidation-Reduction reactions, in the presence of aerobic conditions, are also important processes affecting speciation of chromium in sediment. Recently, natural attenuation conducted on marine dredged sediments showed that there was a formation of hexavalent chromium after two months aging [18]. The storage of contaminated sediments can release metals in surface or subsurface waters and provoke toxic effects on living organisms [19]. In this context, it is necessary to provide treatment techniques that are technically effective and economically feasible for immobilizing contaminants in sediments. In this paper, we propose to study the possibility to use inorganic additives such as hematite and kaolinite, as stabilization agents for metals in polluted sediment.

Several technologies exist for remediation of such pollutants that fall into two general approaches: In situ and Ex situ remediation technology [8,20, 21]. For each technology, distinct categories of the sediment decontamination process including pre-treatment technologies and treatment technologies. Pre-treatment of the sediment typically involves removal of oversized materials and dewatering prior to treating the contaminated sediment. Treatment of the sediment involves application of the primary decontamination process (e.g., Physicochemical, Biological, and Thermal) to reduce, destroy, or immobilize the target contaminants present in the sediments. Treatment may include use of a single technology or use of multiple technologies in order to address the widely-varying contamination and sediment types. The physicochemical treatments are based on physicochemical interactions to destroy, immobilize or separate the contamination. In the physical processes the phase transfer of pollutants is induced. In the chemical processes the chemical structure (and then the behaviour) of the pollutants is changed by means of chemical reactions to produce less toxic or better separable compounds from the solid matrix. Biological technologies generally apply activities of microorganism such as bacteria for the treatment. Thermal processes are based on the stabilization of the pollutants in the sediments in order they are immobile and of the inertizationthe mineral matrices by heating.

The use of phosphate is a common method to reduce the mobility of heavy metals in sediments and soils. Solvay (a Belgian international company) has developed such a technology (The Novosol® Process) to immobilize metal contaminants into hydroxyapatite ($M_5(PO_4)_3OH$, M: divalent metal) and decomposed organic pollutants [22]. However, this process has limitations on the mobility of contaminants such as arsenic and chromium [23, 24].

The aim of the present work was to investigate the adsorption of chromium onnatural adsorbents as potential binding agents for the remediation of the polluted sediment. These adsorbent materials were chosen on the basis of their availability, potential efficiency and market-price. Also these adsorbents generally form one of the more important mineral components in the soils and marine dredged sediments as far as adsorption is concerned. For this reason we decided to study these minerals and use it as an additive for the immobilization of metals in dredged sediment. In addition, chromium mobility is determined in the dredged sediment, before and after adding commercial adsorbent, in order to determine the potential of this material for retaining heavy metals in the dredged sediment.

2. Experimental

2.1. Sampling location of the sediments

Sediments used for the experimental tests were dredged from two ports in northern Morocco: Tangier city port and Larache port (Fig. 1).

Fig. 1. Map of northern Morocco with the sampling locations.

The port of Tangier city is located in the western part of the Tangier Bay, at the entry of the Straits of Gibraltar. It has an area of about 109 km^2 and is composed of an inner region for fishing and tourism activities, a great basin for trading and travelers, and, a free economic zone.

The fishing port of Larache, 90 km south of Tangier and 180 km north of Rabat, occupies the left bank of the Loukkos River and covers an area of 89 ha.

The sediments were immediately transported to the laboratory in plastic bags and stored at a temperature of 4°C prior to analysis.

2.2. Analytical methods

All samples, mixed and homogenized in the laboratory, were dried (40-50 °C), and passed through a 2 mm sieve. After, were stored at room temperature (25 °C) in plastic bags until required.

The reagents used were of analytical grade. $K_2Cr_2O_7$(purity equal to 99.5%), HNO_3 (69 % and d = 1.42), NaOH (purity ≥ 97.0), H_2O_2 (30 % (w/w) in H_2O), HF (purity to equal 48.9 %) and $NaNO_3$(purity ≥ 99.0 %) were supplied by Sigma-Aldrich and were used without further purification. All the solutions were prepared in Milli-Q water. The pH measurements were made with WTW pH meter electrode calibrated with pH buffer solutions (pH 4.00, 7.01 and 10.00) at room temperature (25 °C).

All glassware and plastic materials used were previously treated for 24 h in 10 % (v:v) nitric acid (HNO_3, 69 % and d = 1.42) and rinsed with Milli-Q water.

2.2.1. Chemical analysis

In order to determine total metal concentrations, 0.25 g ofthe sediments were digested with a mixture of nitric acid (HNO_3, 69%), oxygen peroxide (H_2O_2, 30%) and fluorhydric acid (HF 48.9%) in a microwave oven. The amount of inorganic pollutants (As,Cr, Cu, Ni, and Zn) was determined via an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Perkin Elmer Optima 7300, French).Major element analyses were obtained via X-ray fluorescence (Philips PW 1480, French).

2.2.2. X-ray diffraction (XRD) analysis

The crystallized fraction of the samples (e.g., quartz, calcite and pyrite) was made via X-ray diffraction using a SIEMENS D-5000 diffractometerequipped with a rear monochromator and using Kα1 (λ ≈1.789 Å) cobalt radiation. This technique is mainly qualitative and can only provide a semi-quantitative indication. The fraction clay mineralssamples (e.g., kaolinite, illite and chlorite) was determined via X-ray diffraction from blades strip oriented normal glycol for 12 hours in vapourpressure and then heated to 490 °C for 4 hours. The samples were scanned between 4 and 84° 2θ and 2 and 36° 2θ for powders and the blades oriented, respectively.

2.3. Solution preparation

The pH was adjusted manually between 2 and 11 for each batches by addition of acid or base (HNO_3 or NaOH) using Micro-pipette.Hexavalent chromium [Cr(VI)] stock solution was prepared from potassium salts of dichromate ($K_2Cr_2O_7$, purity equal to 99.5 %).A series of standard metal solution were prepared by appropriate dilution of the stock metal solution. $NaNO_3$was used as the supporting electrolyte to maintain the ionic strength (0.01, 0.05 and 0.1 M) constant during the adsorption experiments.

2.4. Batch adsorption experiment

Batch adsorption experiments were performed at room temperature (25 °C) on a rotary shaker at 50 rpm using 50 mL polypropylene centrifuge tubes containing 0.1 mg/L of metal ion solutions and 0.2 g of adsorbents, the contact time was 24 h for Kaolinite [25], and 3 h for Hematite [9]. After agitation, the suspensions were centrifuged at 3000 rpm for 10 min, filtered, acidified and kept foranalyses using an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Various conditions, including the pH (2-11)and the ionic strength (0.01, 0.05 and 0.1 M), were tested.

To obtain adsorption isotherm, the adsorbents (0.2 g) was suspended in hexavalent chromium solutions (concentration range 0.1-16 mg/L) at room temperature and fixed background electrolyte concentration (0.01 M). The pH of the system was maintained at 8, characteristic of the pH value for sediment equilibrated with water. After that, the samples were shaken; the suspensions were centrifuged, filtered and acidified for later analyses of metal ion concentration.

The amount of hexavalent chromium adsorbed was determined from the difference in metal ion concentration measured by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) in the aqueous sample before and after contact.

2.5. Laboratory treatment conditions

The samples were subjected to leaching in batch experiments with and without the addition of the hematite and kaolinite. Leaching experiments were performed using Milli-Q water at a water sample ratio of 10 L/kg. The mixtures were stirred continuously for 24 h, filtered and acidified for analysis. The leachates were analysed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

3. Results and discussion

3.1. Total chemical analysis and mineralogical

The contents of total metal concentrations in raw sediments are presented in Table 1 and compared to the criteria proposed by the French decree of 14 June 2000 [26]. Below level N1, the potential impact is regarded, in principle, neutral or negligible. Between levels N1 and N2, further investigations may prove necessary depending on the project considered and on the extent to which action level N1 is exceeded. Beyond N2 level, additional investigation is generally necessary since significant indices suggest a potentially harmful impact of the operations. It appears that these raw sediments can be considered polluted, mainly in Cr, Cu, Zn, and Ni.

Table 1

Total concentrations of heavy metals in raw sediments in mg/kg on dry material, and comparison with the levels: N 1 and N 2

Element	Sediment from Tangier city	Sediment from Larache	Level N 1	Level N 2
As	9.5	7.7	25	50
Cr	100.8	144.1	90	180
Cu	246.9	33.2	45	90
Ni	46.7	30	37	74
Zn	459.2	103.2	276	552

As shown in Table 1, we can observe that the raw sediment from Tangier city port, exhibit high concentration of Cu (247 mg/kg) that largely exceed level N 2, which is equal to 90 mg/kg. For Cr, Zn and Ni the concentrations are between the levels N 1 and N 2. In the sediment dredged from Larache port, the Cr concentration is between levels N 1 and N 2 but the other elements are below level N 1. Comparison of concentrations of metal in the raw sediments allows concluding that the sediment dredged of Tangier city port displayed a higher contamination than the raw sediment of Larache port. These results emphasize that the raw sediments are polluted and could have to be treated according to levels N 1 and N 2.

Major elements analyses (Table 2) suggest that samples present of high concentrations in Fe- and Al-oxides, which are commonly found in natural soils and sediments as reactive, high surface area, secondary mineral coatings. The Fe- and Al-oxides are known to exhibit a great sorption affinity for Cr(VI) [27]. Despite this high Fe contents as observed in X-ray fluorescence (XRF) analysis, no Fe oxide peaks were detected in X-ray diffraction (XRD) analysis of samples, indicating that most of the iron inraw sediments may be in the amorphous form.

Table 2

Major elements content (oxide %) for the raw sediments

Majors elements	Sediment from Tangier city	Sediment from Larache
SiO_2	48.5	49.6
Al_2O_3	11.9	14.5
Fe_2O_3	7.4	9.1
CaO	11.7	11.2
MgO	1.2	0.5
K_2O	1.7	1.7
Na_2O	2.0	2.0

Based on XRD data (Table 3), the raw sediments are mainly composed by quartz, calciteand clay minerals. Pyrite, halite, aragonite and dolomite are present in minor amounts. The XRD analyses also suggest that the major clay mineral in raw sediments was kaolinite.For this reason we decided to study these adsorbents (hematite and kaolinite) and to investigate the possibility of use them as an additive for the immobilization of metals in a polluted sediment.

Table 3

Mineral and clay mineralogy of the raw sediments

	Sediment from Tangier city	Sediment from Larache
Mineral	Quartz (20%)	Quartz (20%)
	Calcite (15%)	Calcite (15%)
	Halite (trace)	Halite (trace)
	Plagioclase (trace)	Plagioclase (trace)
	Pyrite (trace)	Aragonite (trace)
	Dolomite (trace)	-
Clay mineralogy	Smectite and chlorite (36%)	Smectite and chlorite (39%)
	Illite and/or mica (11%)	Illite and/or mica (7%)
	Kaolinite (53%)	Kaolinite (54%)

3.2. Hexavalent chromium adsorption

3.2.1. Hexavalent chromium adsorption as a function of ionic strength and pH

Experiments were performed to study the effects of pH (2-11) and three values of ionic strengths (0.01, 0.05 and 0.1 M $NaNO_3$) on hexavalent chromium adsorption (Fig. 2). It is evident that the adsorption characteristics are highly pH dependent for hematite, and less for kaolinite. The optimum adsorption is at pH ≤ 4 for Kaolinite (Fig. 2A) and pH ≤ 5 for hematite (Fig. 2B) while the adsorption of hexavalent chromium decreases as solution pH increased. High adsorption of hexavalent chromium at low pH can be explained by the species of the chromium and the adsorbents surface [9, 28-30].

The data presented in Fig. 2 indicate that a significant amount of Cr (VI) is adsorbed on these adsorbents for pH values higher than the point of zero charge of the adsorbents (pH_{PZC} = 8.1 and 4.6 for hematite and kaolinite, respectively). Stummet al. [31] noted that the position of the sharp decrease of sorption is not necessarily related to the value from the point of zero charge and the surface charge, because the free enthalpy of adsorption of an anion on a surface is a combination of electrostatic and chemical effects.

As seen in Fig. 2, better effectiveness of kaolinite was at acidic pH. Although it is be not as satisfactory as that obtained for hematite. This can be explained by the fact that the masse of kaolinite can be considered a limiting factor in the determination of chromium. Indeed, it is possible that the ratio (m/V = 4 g/L) chosen for these experiments is not sufficient to adsorb more chromium.

Hexavalent chromium adsorption increases with increasing ionic strength, especially at higher pH values (Fig. 2 (A)).

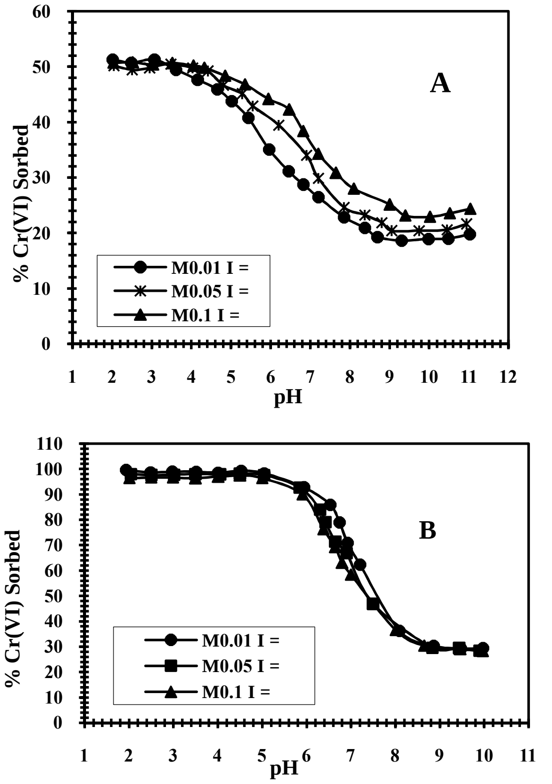

Fig. 2. Adsorption of hexavalent chromium onto kaolinite (A) and hematite (B) as a function of pH at different ionic strengths.

The possible explanation for the observedbehavior is related to the surface charge characteristics of the kaolinite surface, specifically, the silanol groups of overall formula (>SiOH) and the permanent negative charge [32, 33]. These negative charges would tend to reduce anion fractional uptake. At the higher ionic strength, more counterions (positively charged ions) would be attracted to the surface, thereby screening the negative surface charge more effectively and allowing more negatively charged ions (anions) to adsorb.

Adsorption of chromium by hematite at different $NaNO_3$ background concentrations is plotted in Fig. 2 (B). The results indicate that Cr(VI) adsorption is independent of ionic strength. The strong pH dependent and ionic strength independent adsorption of Cr(VI) to hematite, suggest that the adsorption of Cr(VI) is mainly dominated by surface complexation [34, 35].

3.2.2. Adsorption isotherm

The distribution of Cr(VI) between the liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the most popular isotherm models. Two empirical models (Langmuir and Freundlich) was used to fitted the experimental data and to give the opportunity to compare the sorbing capacities of the two tested solids. The data was well fitted to Freundlich equation in linear form.The Freundlich equation has the following form:

$$\log \boldsymbol{q_e} = \log \boldsymbol{K_f} + (\mathbf{1}|\boldsymbol{n}) \log \boldsymbol{C_e}$$

where q_e is the amount of solute adsorbed per unit weight (mg/g) of the adsorbent used, C_e is the equilibrium solute concentration in the solution (mg/L) and K_f and n are the constants representing the adsorption capacity (mg/g) and intensity of adsorbent, respectively. The values of K_f and n were obtained from the slope and intercept of a plot of $\log q_e$ versus $\log C_e$(Fig. 3) and are reported in Table 4. Both of the parameters K_f and n affect the adsorption isotherm. Values of n larger than 1 show the favorable nature of adsorption. The value of n (Table 4) suggests that hexavalent chromium is favorably adsorbed by the Kaolinite and Hematite surface.

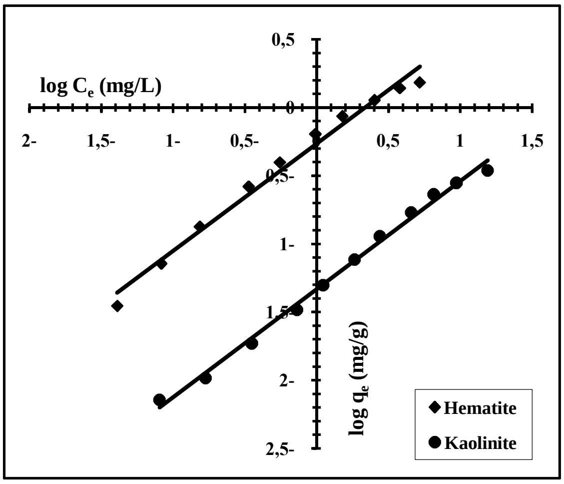

Fig. 3. Freundlich adsorption isotherm at room temperature and pH 8 for Cr(VI) on the adsorbents.

Table 4

Freundlich isotherm constants

Adsorbent	Freundlich		
	K_f (mg/g)	*n*	*R²*
Hematite	0.554	1.272	0.985
kaolinite	0.047	1.262	0.995

3.3. Effectiveness of the chemical treatment

The effectiveness of additives for heavy metals immobilization in the raw sediments was tested in batch experiments. Table 5 shows the concentrations (mg/kg) of metals leached into the solution phase from the raw sediments in the absence or presence of hematite and kaolinite.

After remediation, the content of heavy metals in two sediments would be analyzed. The chemical treatment results show that the additives all could decrease the content in leachates heavy metal of two sediments. Thus, Fig. 2 indicates that Cr(VI) can sorb en hematite and kaolinite, what can explain the results shown in table 5, when lixiviation of Cr(VI) decreases when sediment enriched with these adjuvants are used.In the sediment from Tangier city, the effect of decreasing As, Cr, Cu, Ni and Zn by hematite was significant. The contents in leachates As, Cr, Cu, Ni and Zn decreased by 36 %, 39 %, 48 %, 20 % and 61 % respectively, comparatively with control. Kaolinite was more effective to reduce mobility of Cu and Ni, the contents in leachates were decreased by 55 % and 50 %, respectively.Asexpected, both solids are able to decrease the amount of pollutant released in the aqueous phase, hematite beingmore efficient for anionic species, and kaolinite being more efficient for cationic species. In both cases, the use of mineral additives gives better results than the NOVOSOL process, which is not efficient enough for anionic species(as an example for Cr: itsmass percentage increased from 30.9 % to 66.6 %) [23, 24].

Table 5

Analysis of heavy metals (mg/Kg) in leachate after leaching tests with and without the addition of additives on raw sediments for L/S = 10

	Sediment from Tangier city			Sedimentfrom Larache		
	Control	Hematite	Kaolinite	Control	Hematite	Kaolinite
% Additives	0	15	15	0	15	15
As	0.205	0.131	0.170	0.080	0.045	0.065
Cr	0.266	0.161	0.200	0.165	0.095	0.120
Cu	0.445	0.230	0.200	0.296	0.203	0.189
Ni	0.060	0.048	0.030	0.062	0.047	0.029
Zn	0.074	0.029	0.044	0.125	0.080	0.010

Compared with the control, about 36 %, 53 % and 92 % ofCu, Ni and Zn were decreased in leachates of sediment from Larache after treatment with kaolinite. Stabilization of As and Cr is less efficient with kaolinite, decreasing contents in leachates by 19 % and 27 %, respectively. Sediment from Larache treated with hematite decreases significantly As, Cr, Cu, Ni and Zn contents in leachates with stabilization of 31 %, 42 %, 31 %, 24 % and 36 %, respectively. The data clearly show that after the sediment is treated with mineral additives, the contents of As, Cr, Cu, Ni and Zn were significantly reduced even if anionic (AsO_4^{2-}, CrO_4^{2-}) and cationic ($Cu2^+$, Ni^{2+}, Zn^{2+}) species are present.

4. Conclusion

Even if chromium is present as a mobile anionic species in water, it can be adsorbed at neutral pH values on the surface of two different solid phases, an iron oxide, hematite, and a clay, kaolinite. This could partially explain the relative high amount of chromium present in some Moroccanharbours (Tangier and Larache), where amorphous iron oxide and kaolinite phases can be present. By increasing the amount of these two sorbing phases into sediment by the addition of pure phases of hematite and kaolinite into the dredged sediments, the amount of chromium released in solution after leaching experiments can be decrease up to 40%. Other pollutants present in sediments (Ni, Cu, As, Zn), present as anionic and cationic species in solution, are also partially trapped by no more than 15% of mineral additives. The results of this work could suggest that adding some mineral additives into dredged polluted sediments can stabilize Cr and other heavy metals into the solid phase, by a trapping adsorption process.

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