Application of some clay minerals to eliminate the hazards of heavy metals in contaminated soils

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Abstract

Soil pollution by heavy metals has serious hazards on microorganism plants, human being and ecological environment. Many approaches have been introduced to overcome the problem of contaminated soils by heavy metals as cadmium, copper and nickel. A laboratory experiment conducted using zeolite and bentonite, three rates on contaminated soils (sandy and clay) with 200ppm of each element. The adsorption and release of element by time (1-14 days) have been recorded. The rate constants of Hoerl's and Elovich kinetic models were determined to compare the effect of adding zeolite and bentonite in three rates on sandy and clay soils. The obtained results indicated that the reaction occurs very fast after adding the remediation material and continuous steady by time. The low rate of the material was very effective in increasing the adsorption of the heavy metals. The release of elements as a result of adding both zeolite and bentonite had the order Cd^{2+} > Cu^{2+} > Ni^{2+}. The role of zeolite is more pronouncing in enhancing the adsorption of the heavy metals more than bentonite due its specific molecular structure and high surface area. Therefore it recommended to be applied as a remediation material in polluted soils by heavy metals.

Key words: zeolite, bentonite, heavy metals, contaminated soils.

1. Introduction

Heavy metal pollution in air and agricultural soils is one of the most important ecological problems in the whole world. The presence of heavy metals in industrial wastewater as a result of many manufacturing process is known to cause detrimental effects on human health and environment. Remediation of polluted sites has become increasingly more important in recent years in most developed countries. Sites contaminated by heavy metals, organic compounds and other pollutants could be represents as sources of contamination for groundwater and potentially harmed the inhabitants in the area. In the last few years many researchers studied new techniques to remove contaminants from soils (Saber et. al., 2012).In this point Esmaeilpour ***et al***. (2015) studied the effects of adsorbent minerals (bentonite, zeolite and sepiolite) on transfer of some heavy metals (i.e., Pb, Zn and Cd) from soil to tissues of sunflower. Treatments included: Non-polluted soil, HM-polluted soil, polluted soil + bentonite, polluted soil + zeolite, and polluted soil + sepiolite. Zeolite addition decreased plant uptake of Zn and Cd by about 12 and 0.21 mg/kg, respectively, while bentonite addition reduced Pb uptake by about 3.05 mg/kg, without any significant difference for the other treatments. On the other hand Hasanabadi *et al* (2015) indicated that zeolite was able to decrease the amount of uptake and transmission of lead and cadmium in plant and with decreasing the harmful effects of these elements cause to increase the growth traits, protein and uptake of nutrient in plant. So, zeolite can be used in order to decrease heavy metals uptake such as lead and cadmium and also improvement of growth of plants in polluted areas. Marzieh (2014) stressed on the bentonite play an important role in the adsorbent of the heavy metals, due to the high density and berry color properties and adsorption played an important role in clarifying water and the addition of natural zeolite will reduce heavy metal pollution significantly. Finally Mojiri *et al* (2015) concluded that, for heavy metals removal from landfill leachate and domestic wastewater, employing the powdered zeolite method was more effective than the application of the traditional activated carbon. The objective of this research work was reducing or eliminating the hazard of heavy metals through the application of available natural clay mineral on contaminated soils.

2. Materials and Methods

The A horizon (0–30 cm) of two cultivated soil types were selected in this study. The first sample was collected from village 62, Al Hamool, Kafr El-Shekh governorate was clayey soil and second one was sandy soil from Abou-Rawash, 6October governorate, Egypt. Soil analyses: for particle size distribution, pH, total soluble salts, total calcium carbonate, and organic matter used standard methods (Black *et al* .1982). Two types of clay minerals remediation materials were used in order to examine the removal of Heavy metals (Cd^{2+},Cu^{2+} and Ni^{2+}) from the soils studied. Natural zeolite (clinoptilolite) and bentonite were supplied by Company A & O of Trading and Al-Ahram Company respectively. Clinoptilolite and bentonite were ground and then sieved to different fractions of which the fraction of 2.5–5.0 mm and dust were used for this study. The applied materials were added to soils at four rates i.e. 0, 15, 20 and 25 g/kg.

2.1Experiment procedure:

Three hundred grams of <2 mm air dry soil samples were treated with the remediation materials. The treated soils were incubated at 60% of their water holding capacity for 14 days under laboratory conditions. After incubation periods soil samples were kinetically analyzed for the studied potential toxic elements desorption.Heavy metals released data were fitted to kinetic models represented empirical equations namely:

1- Hoerl equation in the form:

q=a\t^b*e^(b*t)

2-The Elovich equation in the form:

q_t = 1/b ln ab + 1/b ln t

Where:

q = the amount of HM desorption in time t

b &b\ = constant represents desorption rate coefficient 9ppm)$^{-1}$.

a &a\ = capacity constant in mg HM kg^{-1}soil.

t = time (min).

The kinetic parameters of the tested equations were calculated for different treatments applied. Different statistical parameters such as regression analysis applied to test the conformity of used models to describe HM released from different treated soils, evaluation of significant differences in rate coefficients and cumulative quantity of metals desorbed after remediation were done using SAS software (SAS institute, 1985).

3. Results and Discussion

The laboratory experiment which was conducted to evaluate the impact of some natural minerals on the adsorption of heavy metals to overcome their hazard on contaminated soils had resulted in valuable data useful in formations. Regarding the effect of zeolite addition on the adsorption of Cd^{2+} (200ppm) added to soils, the adsorption on sandy soil is obviously lower than clay soil. Fig 1.illustrate the concentration of element released from soil as affected by three rates of zeolite or bentonite (0.15, 20 and 25g/Kg). As a time factor on the reaction, it starts fast in the first few minutes and continues in a steady state until 14 days. Applying three rates of zeolite or bentonite has insignificant impact on the adsorption of the heavy metal in both sandy and clay soils. The adsorption process of Cu^{2+} showed that the influence of bentonite is slightly higher than zeolite on sandy sample, while in clay sample no differences can be detected. With respect to the Ni^{2+} element, the release in sandy soil as affected by zeolite and bentonite is more in control than the three rates of mineral. The adsorption of Ni on clay is very high in all treatments; the concentration of released element is ranging between 40 and 80 ppm in both zeolite and bentonite.

The kinetic equations of Elovich and Hoerl models were applied to describe the reaction of adsorption and release of heavy metals through the treatment with zeolite and bentonite. The data indicated that R^2 (the coefficient of determination) of Elovich equation ranged between 0.99-0.97, while the respective values of Hoerl equation were 0.97-0.92 in sandy soil indicating the Cd^{2+} released. The rate of Cd^{2+} desorbed as expressed by the slope values of constant (b) in kinetic equations, were significantly influenced by soil type and slightly by the rate of zeolite or bentonite. In clay sample, the addition of 25g/Kg of bentonite led to decrease the rate constant from 19.21 in control to 15.40 in treated sample. The same values in sandy polluted sample decreased from 15.61in control to 12.92. The capacity factor (a) in Elovich model reached 16.13 while in sandy treated sample with bentonite (25g/Kg) was 8.72.In Hoerl model, unlike Elovich equation, there is a reverse tend represented in increasing the rate constant of Cd^{2+} release with increasing bentonite or zeolite rates in both types of soils. Regarding the influence of remediation material to contaminated samples, it's found that the rate constant of Cu^{2+} desorption decreased by about 50% compared to control at low concentration of zeolite. Table 5 indicated that zeolite decreased the Cu^{2+} desorption from 18.50 to 9.13 in clay sample and from 8.02 to 4.95 in sandy sample. At low rates of applied bentonite Cu^{2+} desorption was decreased by about 35% compared to control. Accordingly, in previous work (Wahba *et al* 2012), indicated that Hoerl model was fitted to explain the data related with HM released to clay minerals or remediated material applied with especial mechanism, while Elovich or any other model showed conformity to describe the kinetic data is suitable to describe the release of pollutants from the soil-remediation material system. Dealing with Ni^{2+} as hazard cares and serious polluted in soil, the application of bentonite led to decrease its desorption. Data in table 6 showed that in Elovich equation, addition of 25g/Kg decreased Ni^{2+} desorption from 17.85 to 7.09 in clay sample and from 5.81 to 4.50 in sandy soil. The addition of zeolite at a rate of 25g/Kg decreased constant of Elovich equation by about 60%. In this point some researchers found that The selectivity of zeolite species, such as clinoptilolite and chabazite, for heavy metals based on the ionic radius and dissociation constant was as in the followingorder: Pb^{2+}> Ni^{2+}> Cu^{2+}> Cd^{2+}> Zn^{2+}> Cr^{3+}> Co^{2+} (Choi *et al*. 2001; Ok *et al*. 2007). Ion exchange of a specific cation was strongly influenced by the presence of competitive cations and complexion reagents such as anions (Inglezakis *et al*. 2003a,b; Inglezakis *et al*. 2005). According to the standard deviation (SD), it can be concluded that both clay minerals are significantly minimized the rate of heavy metals release in the order Cd^{2+} > Cu^{2+} > Ni^{2+}. It was obvious from the obtained results that the rate of zeolite in reducing the heavy metals release was more pronounced than bentonite.

4. Conclusions

The contribution of the conducted experiment to evaluate the role of zeolite and bentonite to eliminate the hazard of Cd^{2+},Cu^{2+} and Ni^{2+} on contaminated soils, had led to an important scientific information which can be outlined in the following points: The reaction between the heavy metals and the clay mineral started very fast within the first minutes and remained steady until the end of experiment, which means that remediation of contaminated soil, did not require long time. From economic point of view, the low rate of mineral (10 or 15 g/Kg) was quite effective in decreasing the release of heavy metals in both sandy and

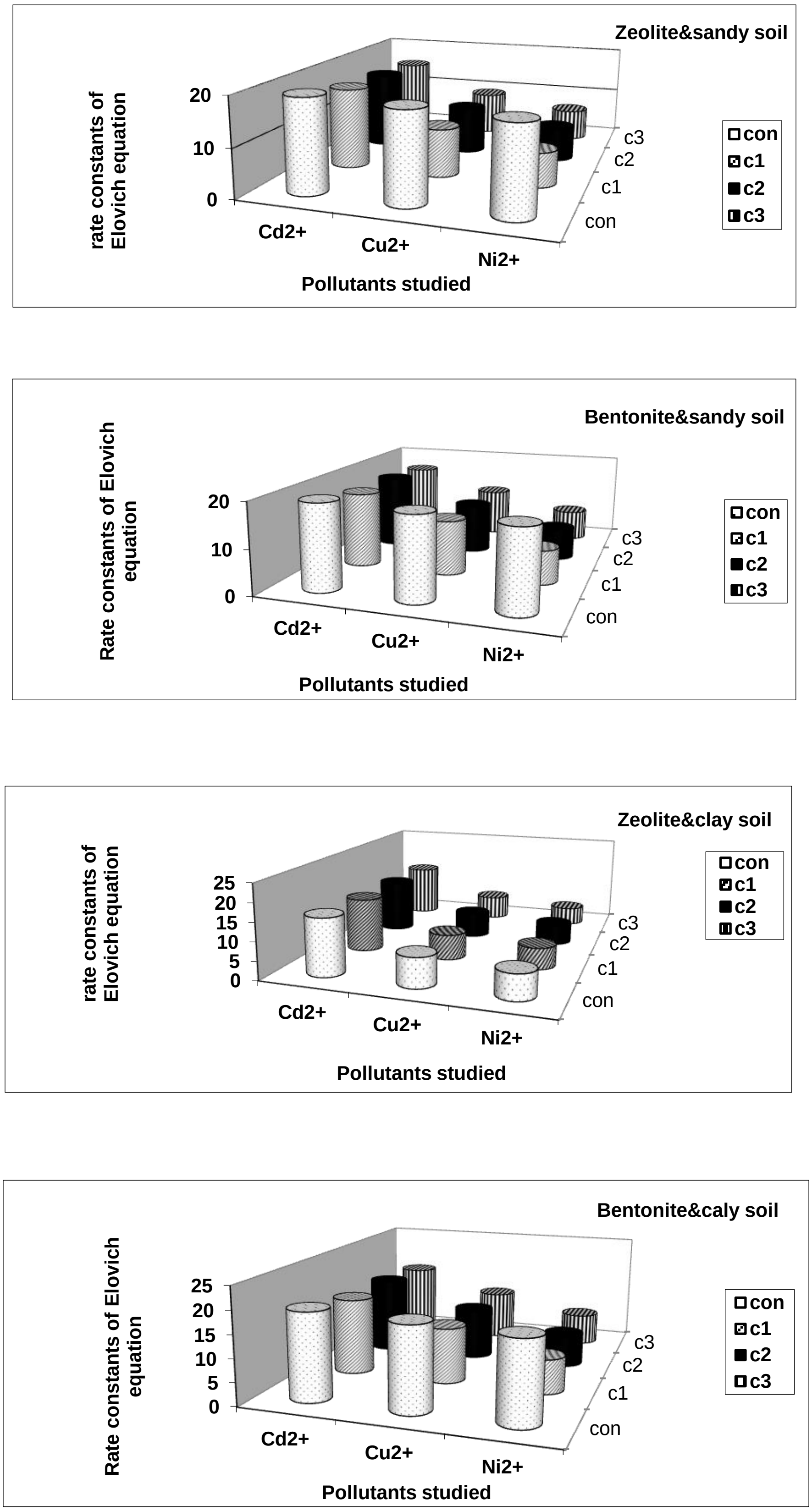

Figure (1) Rate constant of Elovich equation represented heavy metals released from sandy and clay soils as affected by remediation materials applied at different rates.

clay soils. The kinetic models of Elovich and Hoerl were very suitable in expressing the adsorption and release of heavy metals as a result of remediation treatments; through the comparison between the constants (R, a, b and SE) in each equation in three heavy metals (Cd^{2+},Cu^{2+} and Ni^{2+}).Addition of zeolite or bentonite were significantly minimized the rate of heavy metals release in the order $Cd^{2+} > Cu^{2+} > Ni^{2+}$, according to the standard deviation (SD) in the kinetic equations in both sandy and clay soils. The role of zeolite, as a remediation material, was more effective on the adsorption of heavy metals than bentonite. This was related to the specific structure of zeolite high cation exchange capacity and large surface area. However, bentonite had certain properties as its ability to form thixotrophic gels with water and relatively high cation exchange capacity which allow the adsorption of heavy metals and reduce their release in soils.

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