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Nano Based Soil Amendments for Heavy Metal Retention in Brown Fields

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Abstract

Remediation of brown fields is a challenge and this paper aimed at quantifying the extent of heavy metal pollution in contaminated soils and used a Nano based amendment to encapsulate it by means of aggregation and agglomeration in the interstices of soil particles making them inert and sorbing them permanently. Cation heavy metals predominantly priority heavy metals in any brown field viz. Cadmium, Nickel and Lead have been studied on three soils representing a steel mill waste site, battery works unit site and an unscientific solid waste dumpsite. The order of sorption of metal ions was Pb>Cd>Ni. The efficiency of material for desorption under-harsh conditions were evaluated using a strong acid, weak acid and chelating agents such as EDTA. It was found that Nano based amended soils retained more than 55% heavy metals even under harsh conditions proving the potential of Nano technology as a superior material.

Keywords: *Brown Fields, Heavy Metal Retention, Nano Calcium Silicate*

1.0 Introduction

Anthropogenic activities have given rise to serious environmental issues and needs immediate remedial steps. The exposure of soils to many pollutants be it organic or inorganic have resulted in soils contaminated to a very high degree losing its ability to perform its natural functions such as agricultural activities and as a material acting as a *via*-media for water percolation and continuing them in the vadose zone and thus releasing it into the ground water. Soils polluted in these regions, the contaminants gets transported through various processes such as diffusion, advection etc. the rate of contaminant transport is very slow and sometimes taking hundreds of years and in some cases happens in a short period of time and is a site specific condition. But once polluted it is very difficult to remediate and such fields are termed as brown fields.

In order to remediate/clean up a brown field, researchers have been experimenting with different soil amendments some are conventional materials such as lime, flyash, blast furnace slag, LD Slag and cement. Similarly non-conventional amendments have also been used such as rice husk ash, almond ash, activated carbon etc. Recently bio-stabilization has been used as a natural remediation technique wherein the bacteria is used as a media to form precipitates of calcium in the presence of urease enzyme and is popularly termed Microbial Induced

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Calcite Precipitation (MICP), due to inherent problems in managing bacteria an enzyme named urease has been used as a replacement to bacteria and is popularised as Enzyme Induced Calcite Precipitation (EICP). The mechanism of remediation in these materials is it undergoes hydrolysis and later forms films or precipitates of calcium and magnesium ions which sorb the contaminants and form stable precipitates. These precipitates are highly sensitive to pH and work well in the alkaline phases but may desorb at the acidic ranges. Also it has been found that over a period of time the organic/humic content in soils interferes with the sorbed contaminants and releases them back into the environment. Hence the efficacy of these amendments is effective for a small period and will relapse after a few months or years or a few seasons. In order to have stability of soil remediation techniques which shall be permanently effective, innovative materials such as Nano based amendments are showing great prospects, it has been found that there is a change in its working mechanism and bypasses many time dependent processes and relies on aggregation and agglomeration of particles encapsulating the contaminants and making them inert. In this paper the efficacy of Nano Calcium Silicate (NCS) amended soils collected from various brown fields has been tested for its desorption efficiency using various chelating agents such as EDTA, acetic acid, and nitric acid[1-8].

2.0 Materials and Methods

2.1 Soils

Four soils representing different typical brown fields were selected and the base line was taken from a virgin soil obtained from a pristine location the campus of HKBK College of Engineering, represented as RS an industrial site the JSW steel plant near Hospet, Bellary district, Karnataka, represented as JSWS, a battery works unit represented as MS, a solid waste dumpsite represented as MPS. The index properties classified all the soils considered as kaolinitic.

2.2 Contaminants

Three heavy metals were under taken for this study Cadmium Cd, Nickel Ni and lead Pb and were Analytical Grade (AR) a concentration of 10mg/kg and 250mg/kg were prepared as artificial contaminants.

2.3 Nano Calcium Silicate (NCS)

Synthesis of NCS was done by mixing calcium nitrate and silica with citric acid which acts as a fuel. The resulting bright white powder is nano calcium silicate and this method in nano synthesis parlance is termed as combustion synthesis.

2.4 Chelants

Desorbing agents or in other words chelating agents were selected with the following molar concentrations of 0.01, 0.1, 0.5 and 1.0 M and keeping an S/L (solid to liquid ratio) of 1:20. (a) Ethylene Di Amine Tetra Acetic acid (EDTA), (b) acetic acid (c) Nitric acid (HNO_3), the metal(s) spiked soil was subjected to desorption testing using different chelants. Also deionised double distilled water was also used for desorption studies as a bench mark value.

2.5 Desorption Test Setup

Soil samples were cured for a period of 30 days, sub samples of cured soils were drawn for desorption tests with different extracting agent with a range of concentration starting from 0 representing deionised double distilled water, 0.1, 0.25, 0.5 and 1 mole for different chelants, they were taken in a 500 mL PTFE - (Poly Tetra Fluoro Ethylene) bottles, and subjected to shaking using ASTM D18, method shaking at a RPM of 30 and over a period of one day and maintaining a solid to liquid ratio of 1:20. The sorbent was was filtered and the residual concentration of the given metal ions in the filtered solution was determined using Atomic Absorption Spectrophotometer (AAS) Perkin Elmer Analyst AA 400 model. Also the pH of the final solution was noted.

The percentage removal efficiency was calculated using the following equation[9-19].

The percentage Desorption efficacy (%) was calculated using the following equation

Desorption efficacy (%) =

$$\frac{Contaminant\ mass\ in\ supernatant\ (C_L V_L)}{Initial\ contaminant\ mass\ in\ soil\ (C_S M_S)} X\ 100$$

where C_L and C_S are the concentration of a contaminant in the supernatant in mg/L and soil in mg/Kg respectively,

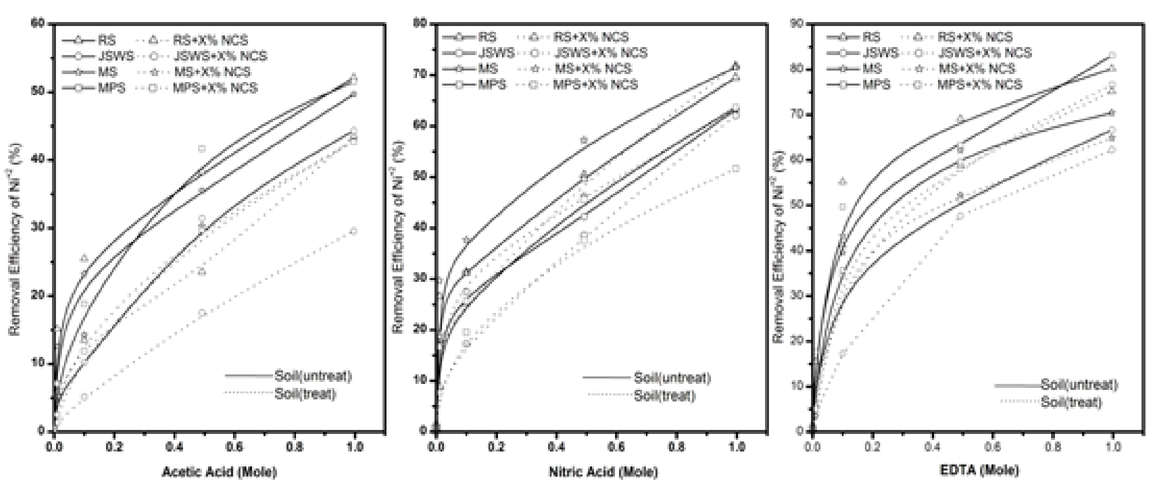
V_L is the volume of supernatant in Litres, and M_S is the dry mass of the soil in Kg.

3.0 Results and Discussions

It can be seen in Figure 1 (which represents untreated/ unamended soil samples) that over a total reaction time of 24 hours the removal efficiency has been monitored, whereas the maximum desorption takes place within an interval of 30 minutes and later gets stabilized. It was observed that more than 80% desorption was taking place at 1 molar concentration of EDTA, and proportionally gets reduced to other extractants. The lowest desorption in general was observed for acetic acid. Cations Cd, Ni and Pb were desorbed to the maximum extent by EDTA, with a range of 71-93% for all molar concentrations, it forms six bonds on a metal ion and forms chelates. Pore fluid pH in soil plays a very important role in desorption, as the pH in the pore fluid reaches the solubility range of the heavy metal ion then desorption becomes dominant. The application of double distilled water was also used as a desorbing agent it showed that all the three metal ions are strongly bound and are not mobile in presence of an aqueous solution. Therefore the removal efficiency was very low, also at a pH acidic range sorption was mostly by ion exchange whereas at an alkaline pH range the sorption was by precipitation. After the experiment the pH of the extracting solution was determined for all molar concentrations of the solutions and it was found that HNO_3 which is a strong acid maintained a pH of 0-2 and acetic acid being a weak acid the pH was at a range of 0-3, Desorption of virgin soils which were non-amended the order was Cd>Ni>Pb. The silanol, alumina and iron are the dominant soil components which play an important role for virgin soils subjected to desorption by various chelating agents.

3.1 Nano based Soil Amendment Subjected to Desorption

The removal efficiency of metal ions was found to be maximum with one molar (1M) EDTA for all the three heavy metals (refer Figure 1). The amendment of soil with NCS saw a drastic reduction in the removal efficiency which means the heavy metals were made inert and sorbed permanently even though a robust desorbing agent in the form of EDTA which shows good efficacy could not do better here in this combination. Only 45% heavy metals were desorbed and this combination retained more than 55% mostly as complexes of EDTA under worst case scenario concentrations of chelants. NCS amended soil retained heavy metals effectively than with only soil and this was probably due to colloids lime soil metal solution forming a separate phase. The dissolving of carbonates and the soil pores getting widened which cascade into increase in pore volume and in turn the soil particle swells giving rise to more sorption sites. As is universal pH always plays a pivotal role in retention cycles and hence the pH played a major role in the retention of heavy metals in the soils. Precipitation is dominant at neutral to alkaline pH while monolayer sorption is explicit at acidic pH, calcium and silica are major constituents of



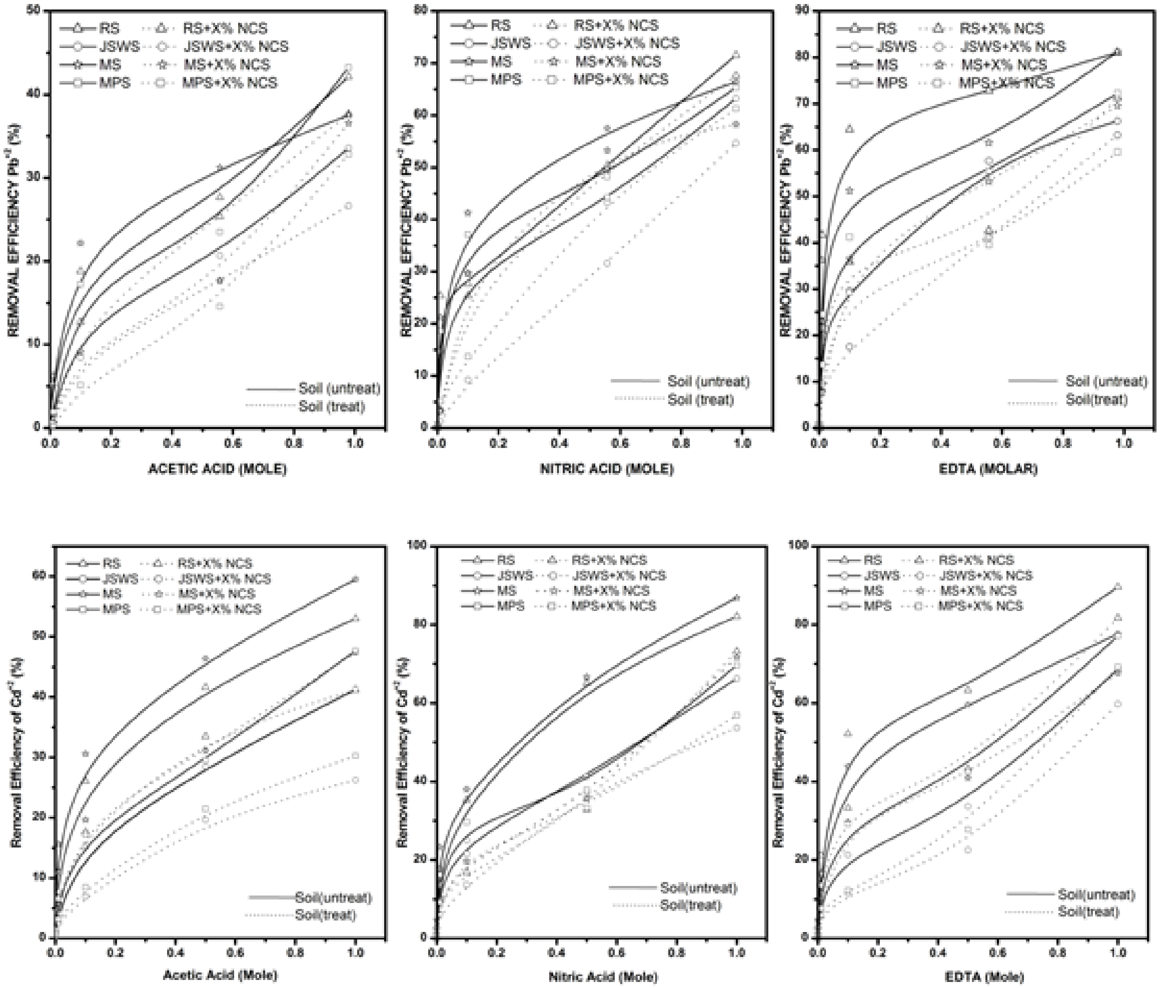


Figure 1. Desorption response of Cd, Pb and Ni for different extractants.

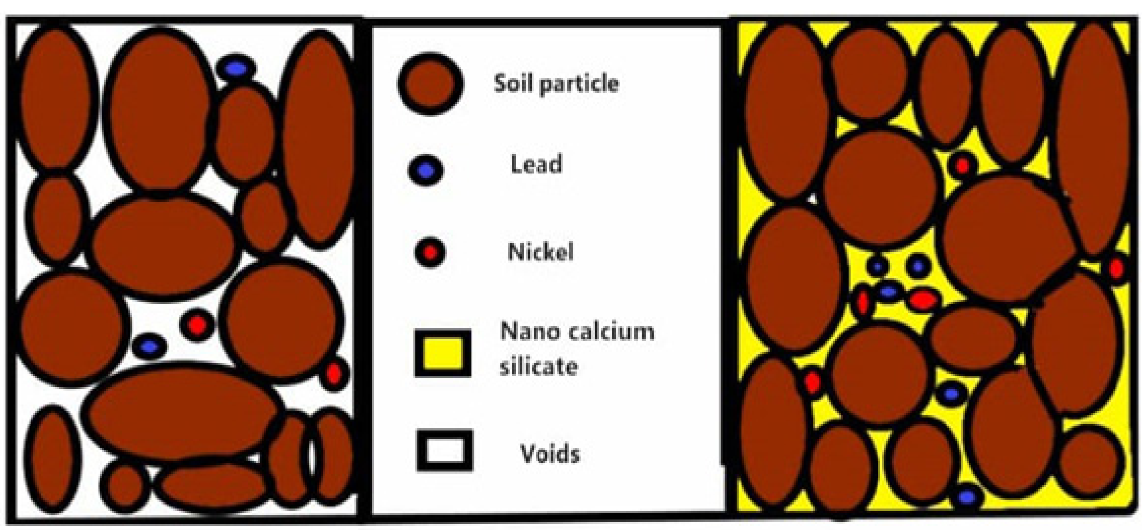


Figure 2. Probable mechanism of entrapment and encapsulation of heavy metals in NCS amended soils.

NCS and are major contributors for stable end products of contaminant retention. The order of desorption for all three heavy metals undertaken in this study confirms to the order Cd>Ni>Pb. Figure 2. Gives a probable mechanism of heavy metal entrapment in the interstices of soils amended with NCS[20-24].

4.0 Conclusions

The efficacy of nano calcium silicate as a nano amendment to retain heavy metals permanently in the interstices of soil particles through agglomeration and aggregation were exhaustively tested through desorption experiments using strong acid, weak acid and chelating agent. It was found that even under harsh desorption conditions NCS was effective in retaining the sorbed metal ions.

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