TITLE : REMEDIATION OF HEAVY METAL CONTAMINATED SOILS USING DIFFERENT AMENDMENT AND DIFFERENT SPECIES OF BRASSICA.

LOCATION : DEPARTMENT OF CHEMISTRY N. R. E. C. COLLEGE, KHURJA

OBJECTIVES :
1. To study the effect of lime, FYM and phosphate on Zn, Cu and Ni adsorption in soils.
2. To screen the possible hyper-accumulators (Brassica Sp.) for decontamination of heavy metal-polluted soils.
3. To study the influence of different hyper-accumulators (Brassica Sp.) on decontamination of heavy metal polluted soils.

IMPORTANCE :

The increasing urban population has prompted a greater significance for urban and peri urban agriculture (UPA). However, metal pollutants are being added to the marginal agricultural lands through sewage; sludge and industrial effluents (Datta et. al. 2000 Rattan et. al. 2002 a)\(^1,2\). This is a matter of concern because of persistence of these metals in soils, uptake by crops and accumulative effects in animals and human beings (Rattan et al. 2002 b)\(^3\). Nevertheless, use of sewage effluents of agriculture lands is on the rise because, besides being a source of irrigation water, these effluents also contain appreciable amount of essential plant nutrients like N, P, K and S etc. (Chhankar et al. 2000 a, b, Rattan et al. 2001.) \(^4,5,6\)
A few measures are suggested for the prevention and control of heavy metal contamination in agricultural soils, which includes i) excavation of soil followed by soil washing and subsequent disposal of treated soils (USEPA, 1991)

(ii) Use of plants which are hyper accumulators of metals like Indian grass (Brassica juncea L) for phytoremediation of polluted soils and.

(iii) Chemical immobilization of heavy metals by the application of ameliorants like lime, farm yard manure (FYM), Phospates, iron oxides, manganese oxides, zeolites etc. among these, soil excavation is the only method for the total removal of heavy metals from contaminated soil. However, it can not be recommended as a viable practice, since it is prohibitively expensive. The phytoremediation also takes a long period to remove a substantial quantity of heavy metals from contaminated soils. Thus, a logical and rational remediation process appears to be to render the metals immobile by using different amendments.

A common method for immobilization of metals in soil is to apply lime, phosphates or organic matter residues to the contaminated sits (Impens et. al, 1991). Addition of other natural or synthetic chemical additives, like zeolites, beringite, hydrous oxides of Al, Fe and Mn, are also known to enhance metal immobility in soils (Gwarek, 1992). However, the application of lime, phosphates and FYM is found to be a promising option for developing countries, as for as the economic constraint of marginal farmers is considered. Soil
pH is reported to be an important factor affecting the mobility and bioavailability of the heavy metals in soil (Evans et. al. 1995)\textsuperscript{12}. Hence, application of agricultural lime is appeared to be a universal treatment for reducing the metal uptake and alleviating the toxicity in different crop species (kukier and chancy, 2000)\textsuperscript{13}. Phosphatic substances like basic slag and rock phosphate are also used as an effective amendment for decreasing the phytoavailability of heavy metals (Mench et. al. 1994)\textsuperscript{14}. Soil organic matter is widely discussed in literature, as a factor controlling the phytoavailability of metals in contaminated soils (chang et al 1997; Hyun et al 1998)\textsuperscript{15,16}

Estimating plant availability of micronutrients and heavy metals is an important objective in soil testing procedures. Such estimates are required in amended soils over different levels of metal enrichment. Single extraction of solid phase metals in soil using selective chemical extratants such as strong chelating agent or a mild neutral salt (Hooda et al. 1967)\textsuperscript{17} has been used to indicate the bioavailability or mobility of heavy metals. Chelating agents such as DTPA(Di - Ethylene tri amine penta acetic acid), EDTA (Ethylene Diamine tetra acetic acid) etc. neutral salts like cacl\textsubscript{2} and dilute mineral acids like 0.1 M Hcl are the most commonly used reagents to assess bioavailable metals in soils (pitchel and salt, 1998)\textsuperscript{18}. However, meager information is available on the usefulness of these chemical extractant in predicting the bioavailable of the metal in amended soils.
Phytoremediation i.e., use of crop plants to absorb and remove metal contaminants from the soil. Some crop plants tend to concentrate a specific metal. Such as one or another of the heavy metals and allow its removal and safe disposal at the time of harvest. The metal extractability and accumulating ability of crop species is also influenced by the addition or presence of soil amendments and complexing agents. The aspects of heavy metal accumulation by crop species particularly in industry waste and sludge amended soil under different soil moisture conditions in the presence of lime and complexing agent have not been extensively studied.

The findings from this study can be utilized for the remediation of heavy metal contaminated soils particularly in the areas of Uttar Pradesh, Tamil Nadu, West Bengal etc. where industry wastes or sewage sludge are being indiscriminately disposed of or added to upland or submerged rice soil for longer time by choosing or making use of specific soil amendment and crop species.

REVIEW OF LITERATURE:

Previous work pertaining to heavy metal contamination through the application of industries waste and sewage effluents and sludge to the soil and its remediation by chemical immobilization and use of Brassica species has been reviewed as summarized below.

The composition of sewage and industrial effluents, i.e. the waste water from urban life and industrial activity, varies with their sources. In general, these effluents are
5. characterized by high BOD, COD and total dissolved salts (chhonkar et al. 2000 a, b). Due to lack of treatment and improper mode of disposal, these effluents cause considerable reduction in dissolved oxygen in water and chemical oxygen demand when such polluted water is used for irrigation, productivity of soil may be seriously affected (Rai and Sharma, 1990). However, now, there is a considerable debate about the application of sewage and industrial effluents to the agricultural land.

Presence of considerable amount of nitrogen, phosphorus and potassium in sewage effluents is reported to be the cause of long-term sustenance of soil fertility in sewage irrigated soils (Dahatonde et. al 1995), Kemppainen (1987), reported that on an average, sewage effluent contained 4.69% dry matter, 2.01 gL⁻¹ total nitrogen, 0.49 gL⁻¹ phosphorus, 5.45 gL⁻¹ potassium and 0.65 gL⁻¹ calcium. According to obbard et al. (1993), the addition of sewage effluents to a soil improves its characteristics and acts as a source of nutrients for crops. Ambika and Latha (1996) found that industrial effluents and domestic sewage outlets contribute to high concentrations of phosphorous in the form of inorganic phosphates and polyphosphates in the water.

Sewage effluents generated out of the mixture of domestic and industrial waste water from different cities have many folds higher heavy metal concentration than that of tube well water (Rattan et al, 2002 a) for example, sewage effluents emanating from ludhiana were reported to contain
710, 6412, 6515, 307, 2.3, 53.1, 357 and 131 μgL⁻¹ of Zn, Cu, Fe, Mn, Cd, Pb, Co and Ni, respectively. The corresponding values for tube well water were 260 μgL⁻¹ for Zn, 70 μgL⁻¹ for Cu, 1550 μgL⁻¹ for Fe, 140 μgL⁻¹ for Mn, 0.55 μgL⁻¹ for Cd, 9.3 μgL⁻¹ for Pb, 75 μgL⁻¹ for Co and 1.5 μgL⁻¹ for Ni.

The increasing heavy metal concentration in soil has attracted many scientists and researchers. Now a days, studies are conducted to find out the causes and remedies for the much discussed problem. Environmental pollution of toxic heavy metals has become an important issue in the present day industrial world. The results of an experiment conducted in USA have revealed that the total concentration of Zn and Cu in air dry soil from certain sites were as high as 11700 and 3420 mgkg⁻¹, respectively (stephen et al. 1998) from 1900 to 1980, industrial emission of Cd, Cu, Pb, Ni and Zn increased by 8, 6, 9, 51 and 8-fold respectively (Nriagu, 1990), carvalho et al. (1991) reported heavy metal contamination of the marine biota along the Rio-de-Janeiro Coast of Southeast Brazil recent estimates revealed that cleaning of US. sites contaminated with heavy metals in USA alone can cost $7.1 billion while mixture of heavy metals and organics bear an additional cost of $35.4 billion for decontaminated (salt et al. 1995), Forstner (1995) reported that of the approximately 1000 contaminated superfund sites identified on the united states environmental protection agency's national priority list of 1986 40% involve heavy metal contamination.
7.

In USA, concentration of Se in agricultural irrigation effluent increased stored soil Se toxic levels in wetland sediments in California, (Banuelas et al, 1997)\textsuperscript{29}. Kashem and Singh (1999)\textsuperscript{30} gave evidences for the heavy metal contamination of soil and vegetation in the vicinity of industries in Bangladesh. Qingren et al. (2000)\textsuperscript{31} reported increasing threat of heavy metal contamination in the soil and crop systems of China.

Remediation refers to process or methods for treating contamination in soil or water such that they are contained, removed, degraded, or rendered less harmful (Pierzinsk et al 2000)\textsuperscript{32}. Use of chemical amendments is one approach for immobilisation of the natural or added metals, lime, FYM and phosphatic fertilizers have been use extensively for detoxification of the dreaded heavy metals in soil plant system. A brief review on each is presented below.

Liming the soils offers a means of minimizing the risk of food chain contamination by reducing the uptake of heavy metals (Smith, 1994)\textsuperscript{33}. Brallier et. al. (1996)\textsuperscript{34} observed reduction in soluble and exchangeable Cd, Ni, and Zn upon liming. Lime application also reduced the uptake of Cd, Ni and Zn in most of the crops but was without any change on Cu uptake. Application of alkaline biosolids to acidic soils was reported to be more effective in reduction of plant uptake of Cd, Cu, Ni and Zn (Brown and Brush 1992)\textsuperscript{35}. However, application of alkaline biosolids on non-acidic soils enhance the Cu content in barely (Lu and Christie, 1998)\textsuperscript{36}. According to Singh et. al. (1989)\textsuperscript{37}. Even in alkaline soils application of CaCO\textsubscript{3} reduced the amount of DTPA extractable Cd as well as
CaCo$_3$ reduced the amount of DTPA extractable Cd as well as tissue Cd concentration of Wheat Kukier and Chaney (2000)$^{13}$ observed that liming reduced Ni concentration by 80, 35-50 and 35% in redbeet, wheat and oat shoots respectively and alleviated the symptoms specific to Ni phyto toxicity in oats (banded chlorosis) studies conducted by Brallier et al. (1996)$^{34}$ indicated that soluble and plant available soil fractions of Cd, Ni and Zn were significantly reduced by liming with an equivalent amount of metal entering highly insoluble fraction which could only be removed by the strong extractants. Thus, several studies indicate that liming might not always have a significant effect; the effectiveness of liming could also very depending on the soil, metals, pH values of limed soil and crop species (Hooda et al - 1997)$^{17}$.

Mench et. al. (1994)$^{14}$ reported that the addition of thomas phosphate basic slag lowered the bioavailable lead content in the metal contaminated soils. Phosphate and phosphate - containing minerals have been shown to reduce bioavailable Pb in soils. The phosphate rock (PR) also effectively immobilized Pb from both aqueous Pb solutions and Pb - contaminated soils (Ma. et. al. 1995)$^{38}$. However, the effectiveness of PR in immobilizing Pb from contaminated soils primarily depends on its ability to provide soluble P in soil solution. According to Ma and Rao (1998)$^{39}$ even though the effectiveness of PR was determined by the soil pH and extent of
contamination. Phosphate aqueous Pb reduction ranging from 21.8 to 100%. The primary mechanism of Pb immobilization in these systems was through the dissolution of hydroxyapatite or phosphate rock and subsequent precipitation of a pyromorphite like mineral (Ma et al. 1995)\textsuperscript{38}.

Ruby et al (1994)\textsuperscript{40} contended that lead was converted to insoluble lead phosphate in a metal contaminated soil containing both phosphorus and lead, and formation of pyromorphite like mineral significantly reduced the Pb bioavailability. Xiao Bing et al. (1997)\textsuperscript{42} the apatite was able to reduce the metal (Zn, Pb) concentration in the leachates to below US, EPA maximum allowable levels, suggesting that apatite could be used as a cost-effective option for remediating metal-contaminated soils metal-organic association in both solution and solid phases by way of complexation and specific absorption are the important mechanisms responsible for rendering the indigenous and applied metals less available for absorption by the plants (karapanagiotis et al. 1991).\textsuperscript{42} De villarroel et al. (1993)\textsuperscript{43} demonstrated that phytoavailability of Cd and Zn in Sewage sludge - treated soil was most likely to be affected by the kinetics of solid-phase metal dissolution. Addition of lime and FYM together in alkaline soils resulted in a significant decrease in the DTPA extracted Cd in soil and Cd content in wheat (Singh et al. 1989)\textsuperscript{37} However, individual application of FYM significantly increased the extractable Cd in soil and Cd content in plant. The predominant role of orgainc matter for Cu adsorption in soils has been reported by Sposito
et al. (1982). Application of FYM is found to decrease the concentration of Zn, Cu and Ni in wheat grain and show (Singh, 1994, Gupta et al. 1989).

Sims and Kline (1991) during their speciation studies of biosolids amended soils, found most of Cu to be associated with organic fraction. During their investigation on the effect of organic matter on the adsorption of Zn and Cu, Borah et al. (1992) found that maximum decrease in adsorption capacities with removal of organic matter was obtained for Cu followed by Zn. However, Miller et al. (1986) clearly showed that the oxide fraction of soil Cu was nearly as large as organic fraction Singh and Oste (2001) indicated that metal adsorption depended on the presence of clay and organic matter, and as a result the soils containing high amount of clay and organic matter showed the highest adsorption for heavy metals.

**DETAILED TECHNICAL PROGRAMME:**

In the present investigation materials used and methods employed are given below:

(1) **Collection and Characterization of Soil:**

A bulk surface (0-15 cm) soil sample will be collected from sewage effluent irrigated field. Soil sample collected will be air-dried, ground and sieved through a 2 mm sieve. This soil will be used for greenhouse study and subsequent chemical analysis.
11.

(2) **Determination of Physicochemical Characteristics:**

(i) **Soil reaction pH** - the pH of soil sample will be determined in 1 : 2 soil water suspension using combined electrode (Glass and Calomel) in a digital pH meter.

(ii) Organic carbon will be determined in soil by wet oxidation method Walkley and Black (1934)

(iii) **Total elemental analysis** - The soil sample will be digested with diacid mixture (hydrofluoric and perchloric acid) in a platinum crucible and subsequently the contents will be dissolved in 6 N HCl as per procedure of Jackson (1967) Zinc, Nickel and Copper Contents in the digests will be determined with flame atomic absorption spectrophotometer (AAS).

**DTPA extractable Zinc, Nickel and Copper**: Soil will be extractable with DTPA solution for available Zn, Cu and Ni as outlined by Lindsay and Norvell (1978).

For extracting to 10 gram air dried soil in polyethylene bottle, 20 ml of extractant will be added and after shaken for 1-2 hours, After filtration the extract will be analyzed for Zn, Cu and Ni with flame Atomic absorption spectrophotometer (AAS)

Green house experiment will be conducted in pots to study the response of Brassica species to the application of Zn, Cu & Ni as well as different amendment in
metal contaminated soil details are given below.

(i) **Metal Levels** : Two
   
   (a) Nil
   (b) 20 mg Zn + 10 mg Cu + 2.5 mg Ni per Kg of Soil

(ii) **Amendments** : Five
   
   (a) Control
   (b) Farm Yard manure (FYM) - well rotten and dried farm yard manure was added at the rate of 10gm per kg of soil
   (c) Single super phosphate (SSP) - Single super phosphate will be added at the rate of 120 Kg $P_2O_5$ per hectare. For this, 332 mg of SSP will be added per Kg. of Soil
   (d) Calcium Carbonate : CaCO$_3$ will be added at the rate of 50 gram per kg. of Soil (5%)
   (e) FYM and CaCO$_3$ - FYM and CaCO$_3$ would be added together at the 10 gm and 50 gm per kg of soil, respectively.
CROP: Five different species of Brassica

1. Brassica Juncea (Indian mustard)
2. Brassica Campestris (Yellow Sarson)
3. Brassica Carinata (Ethiopian Mustard)
4. Brassica napus (Gobi Sarson)
5. Brassica Nigra (Banarasi Rai)

3. Replication: Three

4. Experimental Design: Completely Randomized Design

5. Soil Sampling Time: Two
   (i) 6 Months later
   (ii) 12 Months later

EXPECTED DURATION OF WORK: Approximately 3 Years

Facilities needed for the work and whether they are available in the institution:

The present research project requires colourimeter, pH meter, atomic absorption spectrophotometer and other equipments for soil and plant studies. All the needed equipment and apparatus are available in the laboratories of department of chemistry (NREC College) Khurja, study by atomic absorption spectrophotometer will be conducted either at IARI New Delhi 12 or at any other institution or Laboratory equipped with AAS.
REFERENCES:


17.

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19.
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Remediation of Heavy Metal Contaminated Soils using different Amendment and Different Species of BRASSICA

SYNOPSIS

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Ch. Charan Singh University, Meerut 2008

Prepared under the Supervision of:

Dr. J. P. Singh
Deptt. Of Chemistry
N. R. E. C. College, Khurja

By:

Kushmander Singh
N. R. E. C. College, Khurja