



RESEARCH ARTICLE

Sorption and desorption of mixed contaminants of B P, Cr and Ni in clay loam and sandy loam soils

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ABSTRACT

Adsorption of mixed contaminants namely Benzo (α) Pyrene BαP, Cr and Ni experimented in clay loam and sandy loam soil for different time interval until 96 hrs. Their adsorptions were tested separately and in combination as BαP 0.1, 0.2 and 0.3, Cr 150, 300, Ni 75 and 150 mg kg⁻¹. Generally, clay loam soil adsorbed them more rather than sandy loam soil and their adsorption was increased with an incremental increase of BαP, Cr and Ni as the shaking time increased and a higher concentration obtained during higher shaking time 96 hrs. The adsorption of Cr, Ni and BαP increases with increases their concentration for instance 65%, 66%, 99% and 46%, 56%, 99% was adsorbed for the treatment Cr300, Ni150 and BαP0.3 for clay loam and sandy loam soil respectively. The percentage increase of Cr in BαP0.3+Cr150, BαP0.3+Cr300 treated soil were 68.0%, 78.7 % and 48%, 49% in clay loam and sandy loam soils respectively during the higher shaking time of 96 hrs. A similar adsorption trend was observed for Ni.

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INTRODUCTION

Mixed contaminations in wastewater discharged soils are now increased due to industrialization and population increase in an urban environment. Benzo α Pyrene (BαP) is one of the toxic polyaromatic hydrocarbon commonly found in the wastewater discharged soil coexisted with heavy metals namely chromium (Cr) and nickel (Ni) (Thavamaniet *al.*, 2012). High molecular weight (252.31 g mol⁻¹), low water solubility (1.5 µg L⁻¹), low adsorption coefficients showed (6.13 K_{ow}), high octanol coefficient (5.12 K_{oc}), high melting point and boiling point of BαP very persistent in environment (229-309 days) and toxic to living biota (Toxic Equivalent Quotient (TEQ): 1). The major sources of PAHs are the incomplete combustion of organic material such as coal, oil and wood. PAHs are not synthesized chemically for industrial purposes. Nevertheless, there are a few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries (Kaminski *et al.*, 2008). Loadings may occur through discharge of industrial effluents and through the accidental release of raw and refined products. The reported PAH concentration was ranging from 1 mg kg⁻¹ to over 300 g kg⁻¹ in soil and sediment (Bamforth and

Singleton, 2005). BαP and contamination heavy metal especially Cr and Ni are reported in sewage irrigated soil reported by Wild and Jones (1991) Azad *et al.*, (1992), Singh and Singh (1994), Rattan *et al.*, (2006), Lawal and Audu (2011). Studying the behavior of Cr and Ni in sewage irrigated soils revealed a safe concentration of the metals. However, the bioavailable concentration of metals exceeds the safe limits (Veeramaniet *al.*, 2006). Bioavailability of these heavy metals is regulated by sorption and desorption behavior on to soil particles. Bioavailabilities of the heavy metals are completely determining the organic chemical substance such as BαP (Ramakrishnanet *al.*, 2011). Hence, this study is indented to experiment with releasing behavior of Cr, Ni and BαP in clay loam and sandy loam soils.

MATERIALS AND METHODS

Kinetic experiment

The kinetic experiment was conducted to know the sorption and desorption behavior of BαP (Benzo α Pyrene) mixed with Cr and Ni in soils. Two soils were taken as experimental soils namely clay loam (CL) and sandy loam (SL) to represent prominent soil types of Tamil Nadu. Three doses of BαP were fixed based on the critical limit set for soil. The critical limit for BαP in the soil is 0.1 mg kg⁻¹ prescribed by the World Health Organization (WHO). Similarly,

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Cr and Ni concentrations were fixed based on their critical concentration set for soil. Two doses of Cr and Ni were fixed namely critical concentration and double the critical concentration. Mixtures of Cr, Ni and B α P were also used to study the sorption and desorption in two different soils with five-time interval as 2 hrs, 8 hrs, 24 hrs, 48 hrs and 96 hrs. The time interval was fixed based on the equilibrium obtained with Cr alone, Ni alone and B α P alone. Equilibrium concentration was obtained between 24 to 48 hrs shaking times however the maximum time interval was fixed up to 96 hrs to know the interaction effect beyond equilibration time. Each experimental unit was triplicated. A controlled randomized block design was employed and data obtained were analyzed for their statistical significance using excel sheet of Microsoft office 2010. Descriptive statistical tools were employed to interpret the data.

Details of the treatment

Adsorption of B α P, Cr and Ni were studied in clay loam and sandy loam soil with the following treatment B α P 0.1, B α P 0.2, B α P 0.3, Cr 300, Cr 150, Ni 75 and Ni 150 mg kg⁻¹ inclusive of control treatment in the kinetic experiment I. The second kinetic experiment (II) experimented with the following treatment as B α P 0.1+Cr 300, B α P 0.2+Cr 300, B α P 0.3+Cr 300, B α P 0.1+Cr 150, B α P 0.2+Cr 150, B α P 0.3+Cr 150, B α P 0.1+Ni 150, B α P 0.2+Ni 150, B α P 0.3+Ni 150, B α P 0.1+Ni 75, B α P 0.2+Ni 75, B α P 0.3+Ni 75 inclusive of control treatment.

Quantification of heavy metals in soil solution

Twenty gram of soils measured were transferred 40 mL of centrifuge tube made up of polypropylene. After adding soil, B α P, Cr and Ni solution were added in the centrifuge tube. The concentration of B α P, Cr and Ni were prepared in MilliQ water. Then the centrifuge tubes were kept in end to end over the shaker and removed them from the shaker during every shaking time over. The content of the tube was centrifuged at 10000 rpm for 20 min to collect clear soil suspension. The suspension was filtered through the Whatman no 42 filter paper. The respective filtrates were collected in clean screw cap container made up of polycarbonate and stored in 4 ° C until analysis of them.

Data analysis

Data collected during the experiments were analyzed using descriptive statistical tools available in the excel sheet of MS office.

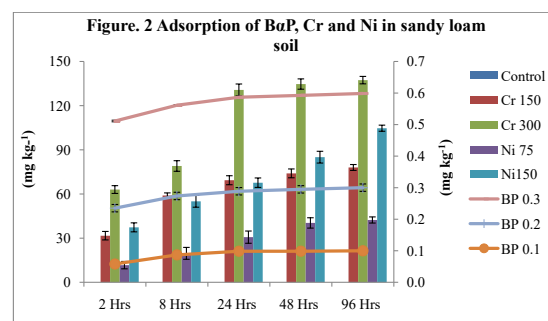
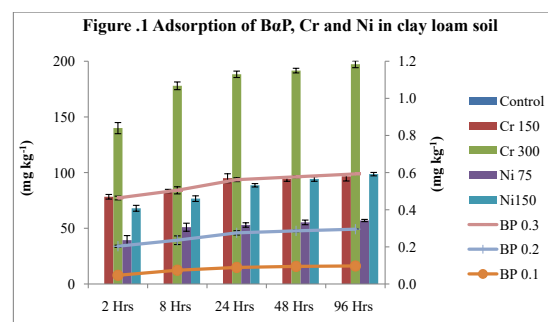
Quantification of B α P in soil solution

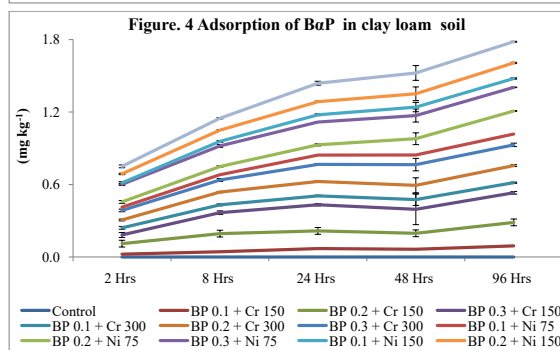
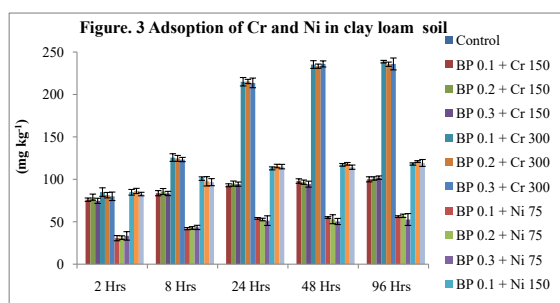
All chemical and reagents were purchased from Sigma Aldrich chemicals. The soil extract (1 to 2 mL) was mixed with methylene chloride (1:1 v/v)

by vigorous shaking for 90 seconds by manually and kept it for 2 h at room temperature before separating the solvent layer. The extracted organic phase was dried over anhydrous sodium sulphate and concentrated to 2 mL by using rotary evaporator. PAHs were analyzed using gas chromatography with ion trap detector (Thermo Scientific) according to the standard method of US EPA 8270 C method. Standard stock solution (1000 ppm) were prepared by dissolving 10 mg of the B α P in 10 mL CH₃CN and stored at -20° C. All working solutions were prepared fresh daily by serial dilution. The PAHs were separated using a 30 m high-resolution capillary column with a 0.25 μ m film. The following temperature regime has been maintained during the analysis as 50° C to 70° C, 70° C to 115° C, 115° C to 175 ° C, 175° C to 300° C, 300° C to 450° C. The calibration was by external standard methods, using a certified B α P (Sigma Aldrich chemicals with 96% purity). The internal standard was anthracene and pyrene used to monitor B α P loss during extraction and clean up. For quality control, experiments on recovery were carried out by spiking a known concentration of B α P (10 and 20 ppm) with contaminated soil. The results showed a significant recovery of 89 \pm 11 %. Percentage of residual standard deviation was carried out by 2% throughout the experiment. The accuracy and precision of the whole chromatographic operation were checked every ten samples by injecting known standard and solvent blank.

RESULTS AND DISCUSSION

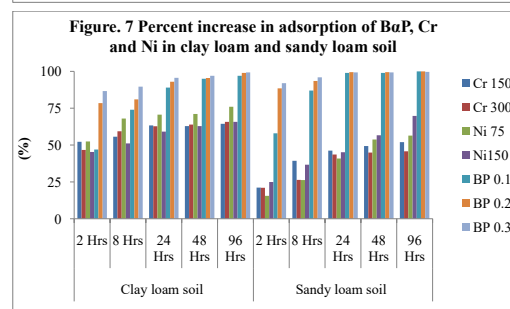
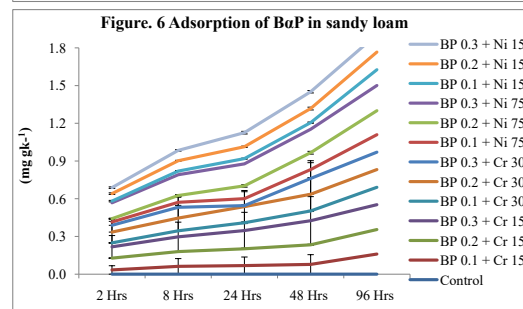
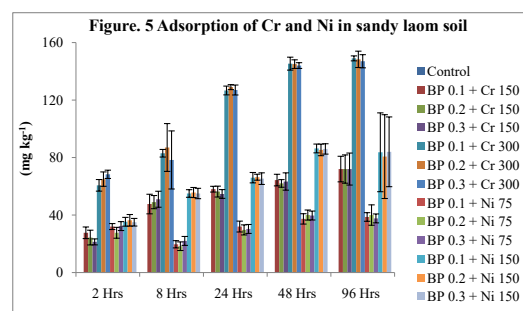
Sewage soil is contamination with a number of organic and inorganic contamination. Among the contaminants chromium (Cr) and nickel (Ni) were





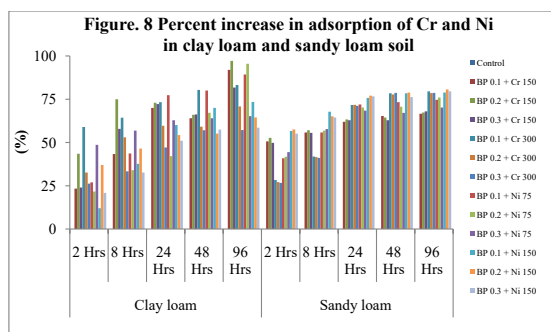
concentrated more than other element and as far as organic contaminants were concerned Poly Aromatic Hydrocarbon (PAHs) was detected more in such soil irrigated with sewage effluent. When the soil was contaminated with BxP along Cr and Ni their releasing behavior in the soil is important as they are sorbed onto soil particles critically determined their availability in soil microorganisms. The present study on adsorption of BxP, Cr and Ni experimented in clay and sandy loam soils showed that adsorption was more on to clay loam rather than sandy loam soil and the quantity of adsorption was increasing with the increasing of shaking time. The maximum adsorption was BxP, Cr and Ni observed in samples of BxP, Cr and Ni and in combination during high shaking time of 96 hrs. (Fig. 1 and 2). There was an incremental increase in adsorption of BxP, Cr and Ni as their spiked concentration was increased. Generally, adsorption of organic chemical substances and inorganic elements on soil particles would take place in active adsorption sites and the chelating process will take place with organic matter. These adsorbent were also tightly bound in the lattice structure of the clay particles. A study on X diffraction revealed that the active adsorption site and lattice structure arrangement were found to be more in clayey soils (Mehdi *et al.*, 2009; Wapakornet *et al.*, 2006; Sarkaret *et al.*, 2012; Weber *et al.*, 1965 and Knight and Tomlinson 1967). The concentration of BxP, Cr and Ni were increased the quantity of adsorption on to clay loam and sandy loam soil was also increased with the shaking time. The adsorption of BxP, Cr and Ni for the treatment Cr300, Ni150 and BxP0.3 increases with increases in concentration were 65%, 66%, 99% and 46%, 56%, 99% respectively for clay loam and sandy loam soil (Fig. 2). In general, the adsorption of Cr and Ni were around 50% and in the case of BxP, they were

completely adsorbed invariably in both the soil type during higher shaking time.

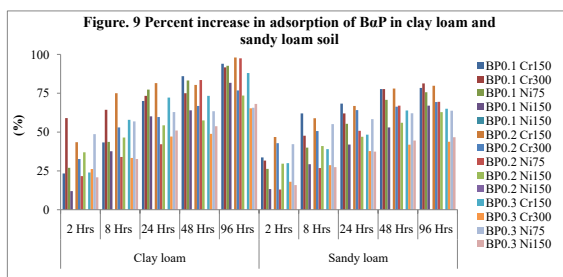


A significant quantity of BxP adsorption was measured when mixed with Cr and Ni in both clay and sandy loam. BxP adsorbed more on to clay loam soil rather than sandy loam soil and this adsorption was more with high shaking time (96 hrs). As the shaking time (between 2 hrs and 96 hrs) increased the quantity of adsorption of BxP was also increased and this increase was more during 96 hrs. With this, an incremental increase in adsorption of these BxP was also measured with BxP concentration. Higher the BxP concentration were higher the adsorption concentration on to soil (Fig. 4 and 6). The adsorption of BxP for the treatment BxP0.3 + Cr150, BxP0.3 + Cr300, BxP0.3 + Ni75, BxP0.3 + Ni150 were 0.245 0.172, 0.196 and 0.196 mg kg⁻¹ and 0.198, 0.138, 0.200 and 0.140 mg kg⁻¹ for clay loam and sandy loam soil respectively (Fig. 4 and 6) and percentage increase in adsorption were 81.3%, 57.2%, 65.2 and 57.4% and 65.0%, 43.8%, 63.0% and 46.7% respectively in clay loams and sandy loam soil (Fig. 9). As far as Cr and Ni were concerned, a similar trend in increase in adsorption of them were measured for their different dose such as Cr 150, 300 and Ni 75, 150 along with BxP 0.1, 0.2 and 0.3 mg kg⁻¹ in both clay loam and sandy loam soils (Fig. 3 and 5). In mixed contamination,

adsorption of both metals namely Cr and Ni were more in clay loam soil rather than sandy loam soils in accordance with the shaking time. As the shaking time increased the quantity of adsorbed Cr and Ni concentration increased. The quantity of Cr was adsorbed more 102.00 (68.0%) and 236.00 (78.7 %) mg kg^{-1} in clay loam soil rather than 72.00 (48%) and 147.00 (49%) mg kg^{-1} in sandy loam soil for the treatment for B α P0.3 + Cr150, B α P0.3 + Cr300 respectively (Fig. 3, 5 and 8) during the shaking time 96 hrs respectively. The quantity of Ni was adsorbed more 52.66 and 119.00 mg kg^{-1}



in clay loam soil rather than 37.67 and 84.00 mg kg^{-1} in sandy loam soil for the treatment of B α P0.3+ Ni75, B α P0.3 + Ni150 respectively (Fig. 3 and 5) and the percentage increase was 70% 79% and 50.20%, 56.0% respectively (Fig. 8). Adsorption of Cr and Ni were decreased during the earlier shaking time for instance during 2 hrs later then be increased and this increase in adsorption of Cr and Ni not influenced by B α P which was spiked in three concentrations namely 0.1, 0.2 and 0.3 mg kg^{-1} . At the end of the shaking time, the maximum adsorption



of Cr and Ni was obtained and as the dose of the Cr (150 and 300 mg kg^{-1}) and Ni (75 and 150 mg kg^{-1}) increased. The adsorption of Cr for Cr 150 and Cr 300 were 66% and 78% and 48% and 49% in clay loams soil were in the case of adsorption of Ni in Ni75 and Ni 150 were 76% and 80% and 50.2% and 56.0% for clay loam and sandy loam soil respectively. As far as B α P was concerned that there were fluctuations in B α P adsorption starts from 43% to 92% for both the doses of Cr in clay loam and sandy loams soil. This fluctuation in B α P adsorption may be the presence of metal cations could decrease the adsorption of synthetic organic chemical substance,

for instance, Cd^{2+} antagonistically interacts with a synthetic organic chemical such as atrazine (Chen *et al.*, 2008). Specific interaction might occur between B α P and soil organic matter (Bradl 2004, Chiou and Kile 1998). Further, the metal cations could bind with OH and COOH of the soil surfaces where metals could occupy the adsorption sites (Sarkaret *et al.*, 2012 and Veeramaniet *et al.*, 2010). And the ratio of charge to the radius of the cation; as bigger the ratio, metal can easily replace the original compound (Chen *et al.*, 2007 and Liu *et al.*, 2012). The radius of the Cr was bigger than Ni gives competition for active adsorption site. However, Cr and Ni were adsorbed similar quantity. When it comes to B α P a maximum of 57% to 96% in clay loam and 44% to 80% in sandy loam soil was adsorbed within 24 hrs and completely absorbed during the end of the shaking time. But, presence of B α P was not significantly affecting the adsorption of Cr and Ni in the present study as their concentration as meager and this was in agreement with Liu *et al.*, 2012 as adsorption of organic chemicals substance (menafcet) was not affecting the metal cation (Cu^{2+}).

CONCLUSION

It can be concluded from the study on adsorption of B α P, Cr and Ni

Adsorptions of B α P, Cr and Ni have increased with the incremental increase of shaking time and this was more during higher shaking time of 96 hrs.

Adsorption of B α P, Cr and Ni was more in the clay loam soil rather than the sandy loam soil

Adsorption of B α P, Cr and Ni was more invariably in both the soil types irrespective of spiking concentration either alone or in combination.

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