Kinetics and isotherm studies for the adsorption of metal ions onto two soil types

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H I G H L I G H T S

- Organic Carbon and Cation Exchange Capacity (CEC) influenced the equilibrium time.
- Removal rate of Cu(II) by red soil was 97.4% and of Ni(II) by black soil was 99.9%.
- Freundlich isotherm model best explained the adsorption process.

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Transport of contaminants from soil to other trophic levels is associated with retention/binding capacity of soil with pollutants. The sorption potential of red and black soils for Cu(II) and Ni(II), respectively was analysed through batch experiments. The batch experiments were conducted to identify equilibrium time, equilibrium adsorbent dosage and equilibrium metal concentration. The kinetics and adsorption isotherms were studied using pseudo-first order and pseudo-second order equation, and Langmuir, Freundlich and Temkin isotherm models. Agitation time, adsorbent dosage and metal concentration played a significant role in the rate of adsorption. The percentage removal of Cu(II) and Ni(II) was higher initially and reached equilibrium after 480 min and 300 min of agitation, respectively. The maximum removal rate for Cu(II) by red soil was 97.3% and for Ni(II) by black soil was 99.9%. The examination of kinetics and adsorption isotherm revealed that the sorption experiments fitted well with the pseudo-second order equation and Freundlich isotherm model, respectively. Thus, red and black soil have significant metal retention potential for Cu(II) and Ni(II), respectively.

1. Introduction

Soil contamination due to heavy metals is one of the associated problems that impacts the life sustaining system. Higher toxicity and mobility in the environment keep heavy metals as priority pollutants (Demirbas, 2008). Metal ions may enter into the soil either through natural pedogenesis or anthropogenic activities (Ma et al., 2010). Soil contamination by natural processes is only specific to the nature of the parent materials and other associated sources. Anthropogenic sources play a major role in adding up significant concentration of heavy metals in soil and adversely impact its life sustaining

characteristics. Though toxic in nature, heavy metals are regularly used in various industrial purposes. Several anthropogenic activities, like disposal of industrial effluents, generation of solid and hazardous wastes, use of pesticides and chemical fertilizers, dispersion of certain air pollutants, etc. contribute to contamination of soil by metals.

The impact of heavy metals is high due to non-degradability in the environment and toxicity (Kumar et al., 2013). Heavy metal retention in soil can cause several long term implications on its physico-chemical, biological characteristics as well as fertility and productivity (Nicholson et al., 2003; Alemayehu and Lennartz, 2010). Metals such as Cu, Ni and Zn can cause severe problems, as they take part in biological turnover (Joner and Leyval, 1997; Antic-Mladenovic et al., 2010). Heavy metals can also get bioaccumulated and transferred into food chain (Burger et al., 2000). The less effective treatment of wastes/effluents containing heavy metals from various sources can cause issues related to health and environment (Dursun, 2006), and is a main cause for soil contamination.

The solubility of heavy metals in soil depends upon its interaction with solid phase. The heavy metals added to the soil may undergo several processes, i.e. (i) adsorption/desorption, (ii) precipitation/dissolution reaction, (iii) plant uptake, (iv) oxidation/reduction, (v) dissolution, and (vi) possible mobility through the soil profile (Sherene, 2010; Ramachandran and D'Souza, 2013). Though these processes can occur concurrently, metal availability and solubility are predominately dependent on adsorption (Sparks, 1999). It implies that the behaviour and bioavailability of metals in soil are affected by adsorption process. Adsorption is related with control of complexes and metal ions in soil and subsequent accumulation by plants (Tangahu et al., 2011). In variety of soil conditions, sorption is the most dominating process as the maximum concentration of metal is associated (adsorbed) with the solid phase (Sherene, 2010). The major environmental issues arise when the metals are mobilized in the soil solution and transported to above ground biomass. Thus, adsorption property of soil is vital in the decline of heavy metals in the environment.

The risk of soil exposure to the pollutants needs regular monitoring. Several conventional treatment technologies are available for soil decontamination (adsorption, chemical reactions, coagulation−flocculation, electrochemical techniques, filtration, flotation, ion exchange, membrane processes, precipitation, sedimentation, etc.) with varying degree of success (Valdes et al., 2004; Deuschle et al., 2008; Marti et al., 2008; Miladinovic and Weatherley, 2008; Abdullah et al., 2009; Delmas et al., 2009; Foo and Hameed, 2009; Liang et al., 2009; Macfarlane et al., 2009; Zhu et al., 2009).

Metal retention capacity of soil is an important parameter to understand (Morera et al., 2000) and evaluate the effective treatment measures (Arias et al., 2006). Thus, metal adsorption capacity of various adsorbents is extensively studied. Morera et al. (2000) studied the sorption and distribution of Cd, Cu, Ni, Pb and Zn on cultivated and uncultivated soils. Yavuz et al. (2003) studied the adsorption of Cu, Ni and Co using kaolinite. Veeresh et al. (2003) studied the adsorption of Ni in three soils of India. Dada et al. (2012) used rice husk for the adsorption of Zn. Mellis et al. (2004) studied the adsorption of Ni by superficial and sub superficial soils and Markiewicz-Patkowska et al. (2005) studied the sorption behaviour of Cd, Cu, Pb and Zn using urban soils. Arias et al. (2006) studied the adsorption of Cu and Zn in acid soils. Jia et al. (2008) examined the adsorption of Cu and tetracycline using Whushan soil and red soil. Ma et al. (2010) examined the adsorption of Cu(II) using paddy soil. Krishna and Swamy (2012) studied the adsorption of Ni through the use of calcinated brick. Ramachandran and D'Souza (2013) studied the sorption of Ni in different Indian soils. Various conventional adsorbents and waste materials, such as activated carbon (Tumin et al., 2008), chitosan immobilized sand (Wan et al., 2004), sour orange residue (Khormaei et al., 2007), spent grain (Lu and Gibb, 2008), neem leaves (Kumar et al., 2013), etc. were studied for the adsorption of Cu(II). For adsorption studies on Ni(II), adsorbents, like dried activated sludge (Aksu et al., 2002), peat (Ho and McKay, 2004), rice bran (Zafar et al., 2007), lignin (Guo et al., 2008), Blue green algal biomass (Parameswari et al., 2009), bael tree leaf (Kumar and Kirthika, 2009), etc. were assessed.

Since, the soil sorption capacity may be associated with environmental contamination; it is quite essential to know the soil's potential to adsorb metals. According to Indian Council of Agricultural Research (ICAR), soils in India fall under eight categories *viz.*, alluvial soils, black cotton soils, red soils, laterite soils, mountainous or forest soils, arid or desert soils, saline and alkaline soils, and peaty and marshy soils. Among these, alluvial soil, red soil and black soil constitute 30.4%, 26.8% and 16.6%, respectively (Bhattacharyya et al., 2013). According to Marbut's system of soil classification, soils fall under three orders *viz.*, zonal, azonal and intrazonal. The red and black soil fall under intrazonal soils. Further, according to US soil taxonomy the red soil and black soil fall under Alfisols and Vertisols order, respectively. The ever increasing industrial, urbanization and agricultural activities in India significantly add heavy metals such as Cu, Ni, Pb, Cd and Zn to the soil. The Cu contamination in soil is largely due to application of chemical fertilizers and compost, and land treatment through industrial waste water. The source of Ni in soil could be both lithogenic and anthropogenic. The major agricultural sources of Ni include phosphatic fertilizers and pesticides. Waste materials from electroplating units, paint manufacturing units, nickel–cadmium batteries, etc. are also known sources of Ni (Mellis et al., 2004). Copper and Ni are known to affect different functional attributes in soil system such as biogeochemical cycling including the carbon dynamics and microbial functioning. Since both these metal are essential for plant metabolism, change in their concentration in soil beyond permissible limit will impact plant growth and development. Various agencies have stipulated permissible limits for heavy metals in soil. For the scope of this paper, we present here the levels as suggested by Directive (1986) which are 50–140 ppm for Cu and 30–75 ppm for Ni. Further, on a regional context Indian standards for Cu and Ni are also available, the permissible limits of which are 135–270 ppm and 75–150 ppm, respectively (Awasthi, 2000).

While most of the Ni contamination studies in soils are restricted to industrialized temperate regions (Al-Hamdan and Reddy, 2006), sub-tropical and tropical regions in Asia have also witnessed few such studies (Ramachandran and D'Souza, 2013). However, studies on Indian soils are limited. Though Ramachandran and D'Souza (2013) attempted to examine