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5- SUMMARY

Three experiments were conducted to (i) evaluate adsorption isotherms of copper by two soils (varied in their texture and calcium carbonate content), pure clay minerals and oxides of Fe and Al,(ii) investigate the effect of pH on adsorption and desorption of copper from the adsorbent materials, and(iii) assess the competitive adsorption of copper and zinc on the tested materials.

Experiment 1:

This experiment was carried out to evaluate adsorption of copper by tow soil samples (sandy loam and sandy clay loam with 11.84 and 21.15%$CaCO_3$,respectively) clay minerals (kaolinite ,bentonite,atapolgite and montmorillonite) and oxides of Fe and Al with and without back -ground of calcium nitrate.

A portion of one gram of each soil sample and 0.1 gram of clay minerals and oxides of Fe and Al were equilibrated for an hour in a 50-mL reaction vessel with a solution of $Cu(NO_3)_2$ having 0-50 µg Cu mL, in presence of $Ca(NO_3)_2$ ranging from 0-0.1 M as a back ground .

The pH of clay minerals and Fe and Al oxides was adjusted to 4 and 6. After equilibrium, Cu content in the filtrate was determined using atomic absorption spectroscopy (AAS) and calculations of adsorbed Cu were done .

Experiment II:

To investigate the desorption of Cu from the adsorbent materials the second experiment was conducted. A portion of one gram of each soil sample was equilibrated with 40 mL of Cu solution having 0-50 µg mL^{-1} in presence of 0.1 M $Ca(NO_3)_2$ ionic strength buffer for 24 h. However, 0.75 gram of each clay mineral and Fe and Al oxides were equilibrated with 300 mLCu solution

having 10μg mL^{-1} in presence of $Ca(NO_3)_2$ as aforementioned after adjusting the pH to be in the range of 4 to 8 with 0.5 unit increment . After shaking samples (10mL each) for 24h, they centrifuged and filtered, 20 mL of 0.005M DTPA solution were added to the settled sample in the centrifuge tubes, shaken for an hour, centrifuged, filtered and Cu concentration in the filtrates was determined using AAS.

Experiment III:

To study the competition between Zn and Cu on the surfaces of soils , clay minerals and Fe and Al oxides , one gram portion from each soil sample and 0.1 gram from each clay mineral and Fe and Al oxides were shaken , after adjusting the pH to be in the range of 4.0 to 7.0 , with 40mL of distilled water containing three different ratios of Cu to Zn concentration (25 μgCu mL^{-1} : 0 μg Zn mL^{-1}, 25 μg Cu mL^{-1} : 25μg Zn mL^{-1} , 50μg Cu mL^{-1} : 25 μg Zn mL^{-1} and 25μg Cu mL^{-1} :50μg Zn mL^{-1}) , as well as 0.1M of $Ca(NO_3)_2$ .The samples were centrifuged at 3000 rpm for 15 min and the supernatants were collected for determination of Cu and Zn by the atomic absorption .

The obtained results could by summarized as follows:

Experiment I :

- Adsorption of Cu on sandy loam and sandy clay loam soils increased as a result of increasing the initial Cu from 0-50μg mL^{-1} under all different concentrations of back –ground $Ca(NO_3)_2$, which were in the inverse direction of Cu adsorption.

-Adsorption maxima of Cu on sandy clay loam soil under different concentrations of $Ca(NO_3)_2$ were higher than the corresponding values obtained with sandy loam soil.

- Significantly, all values of adsorbed Cu on the soil sample were fitted to both Langmuir and Freundlich isotherms for back-ground electrolyte of 0.0,0.001,0.01 and 0. 1M $Ca(NO_3)_2$.

-In the tested soils there was an increase in Cu adsorption ($\mu g\ g^{-1}$)with increasing the equilibrium pH from 4.0 to 7.0 with 0.5 unit increment.

- Adsorbed Cu on kaolinite , bentonite, atapolgite and montmorillonite, to great extent, was gradually increased with increasing initial concentrations of Cu from 0 to 50 $\mu g\ mL^{-1}$, such increase was more pronounced at pH 6.0 as compared to pH 4.0 .

- Adsorption of Cu on both kaolinite and bentonite did not fit Langmuir isotherms at pH 4.0. However, at pH 6.0, data were fitted to Langmuir isotherms with r^2 values of 0.537** and 0.904*** respectively. But in case of atapolgite and montmorillonite, the adsorption data were not fitted.

-Adsorption of Cu on all clay minerals significantly obeyed Freundlich isotherms at pH 4.0 and pH 6.0. However, in case of montmorillonite, a poor relationship was observed between adsorption isotherms and Freundlich equation at pH 4.0.

-Adsorbed Cu on Al and Fe oxides gradually increased with increasing the initial concentration of Cu at all tested pH values, especially pH 6.0 where highest adsorption was encountered.

- Adsorption data of Cu on Al oxide at pH 6.0 obeyed Langmuir isotherms contrary to that obtained at pH 4.0. However, in case of Fe oxide, poor relationships were observed between equilibrium

concentration and adsorbed Cu, as well as data did not obey Langmuir isotherms.

-Copper adsorption on Al and Fe oxides was significantly fitted to Freundlich equation at both pH 4.0 and 6.0.

-The maxium desorption percentages of Cu with DTPA solution were 62 and 73 for sandy loam and sandy clay loam soils, respectively.

-Increasing pH values of DTPA solution > 6.5 significantly increased the amount of desorbed Cu from clay minerals.

-Increasing pH values of the DTPA solution from 4.0 to 6.0 decreased the desorbed Cu from Al and Fe oxides. With increasing pH > 6.5, the amounts of desorbed Cu were increased.

-The preference of the soil adsorbent to Cu over Zn was indicated when they added together as Cu adsorbed % was increased gradually with increasing pH with slight difference as compared with no Zn addition. However, the adsorption of Zn was more affected by Cu.

-The affinity of atapolgite to Cu was affected largely by pH and by Cu concentration in the equilibrium solution.

-Less amounts of Zn were adsorbed on montmorillonite and bentonite as compared to Cu indicating the preference of montmorillonite to Cu.

-The highest Cu adsorption on Al and Fe oxides was achieved with 2:1 Cu : Zn ratio and Cu adsorption on such oxides was increased with increasing pH and its initial concentration.