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Effect of paper mill sludge on adsorption and desorption of Cd(Ⅱ) and Pb(Ⅱ) in paddy soils

Yan Liu [1, a], Pei-qin Peng [1,*], Xiao-long Zhu, Xian-qing Ding

[1]Research Center for Environmental Science and Engineering,

Central South University of Forestry and Technology, Changsha 410004, China

[a]lyyan1221@163.com

[*] Corresponding author:Pei-qin Peng. Tel.:+0- Tel:0371-85623459; E-mail:pqpeng123@sina.com

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Abstract. There are high organic matter and cation exchange capacity (CEC) in paper mill sludge, which can be used efficiently to amend soil properties and promote the growth of crops. The batch method was used to investigate effects of paper sludge on adsorption and desorption of Cd(Ⅱ) and Pb(Ⅱ) in two types paddy soil(red soil, purple soil), through adding paper sludge to red soil and purple soil. The results showed that isothermal sorption process of Cd(Ⅱ) and Pb(Ⅱ) by soils and paper sludge could be well described by Langmuir equation and Freundlich equation, and all coefficients(*r*) were higher than 0.9. The purple soil had a higher sorption capacity of Cd(Ⅱ) and Pb(Ⅱ) than red soil. The sorption capacities of Cd(Ⅱ) and Pb(Ⅱ) in soils increased after added paper sludge, and they reached adsorption equilibrium as the percentages of paper sludge were 10%, 1% in red soil and purple soil, respectively. The desorption capacities of Cd(Ⅱ) and Pb(Ⅱ) in soils decreased after added paper sludge, and they reached minimum as the percentages of paper sludge were 5%, 2% in red soil and purple soil, respectively. It was better to immobilize Cd(Ⅱ) and Pb(Ⅱ) after added paper sludge, thus paper mill sludge can relieve the migration of heavy metals in soil-crop systems. It can provide a new way for safe using of heavy metal contaminated soil and resource utilization of paper sludge.

Introduction

Soil heavy metal pollution is not only extremely difficult to eliminate, but also has a hidden, long term and nonreversible features [1]. Soil is increasingly being seen as a major source of metals reaching food chain, mainly through plant uptake [2,3]. As two common heavy metal contaminants in soil, cadmium and lead are in dynamic equilibrium of adsorption and desorption, after entering the soil. These balances control the bioavailability of cadmium and lead in soil and impact their migration into the food chain [4].

Studies had shown that paper mill sludge was rich in organic matter and N, P, K and other nutrients [5,6], which can be used efficiently to amend soil properties and immobilize heavy metals in soil, respectively[7,8]. Paper sludge had been used in agriculture as an organic matter [9,10].In addition, some studies had examined paper sludge can be used available in some other fields, such as building, chemical materials, and so on[11,12,13]. And M.Hojamberdiev indicated that paper sludge was a low cost, highly effective sorbents with organic fibers and inorganic fillers (kaolinite ($Al_2Si_2O_5(OH)_4$), calcite($CaCO_3$) and talc($Mg_3Si_4O_{10}(OH)_2$))[14]. However, There are fewer researches on whether paper mill sludge improves soil heavy metal pollution or not.

In this study, take the paddy soils that developed from red soil and purple soil parent materials as research object and study adsorption and desorption behavior of Cd, Pb in different soils. The adsorption and desorption of Cd, Pb in soil with paper sludge addition was investigated to demonstrate the emendation of paper sludge to contaminated soil. It attempts to clear the influence of paper sludge land application on adsorption of heavy metals in the soil desorption process , and

provide a scientific basis for the utilization of heavy metal contaminated soil and the safe using of paper sludge .

Materials and methods

2.1 samples and analytical methods

The soils (red soil, purple soil) were collected form the topsoil layer (0-20cm) of paddy soils, Hunan Province, China, where were uncontaminated by heavy metals. Paper sludge was dewatered sludge, provided by Green paper mill, where located in Yue-yang city, Hunan, China. After being air-dried and the samples were passed through a 2mm-mesh sieve and stored in plastic cans.

The pH values of soils and sludge were measured in 1:5 soil to water ratio, and determined by pH meter (pHS-3C). Organic matter was determined by the $K_2Cr_2O_7$ method [15]. CEC was determined by $BaCl_2$-H_2SO_4 method. Total nitrogen, phosphorus and available nitrogen were determined according to standard laboratory methods [16].The contents of Cd and Pb were quantified by atomic absorption spectrophotometry [17] (Z-2000, Japan). Percentages of sand, silt and clay were determined by the wet sieving method and the pipette method. All these analyses were performed in duplicate.

2.2 Adsorption experiments

Adsorption experiments of soils, paper sludge: Air-dried samples (2.500 g) were equilibrated for 24 h at (25±1) ℃ in 20 mL of 0, 10, 20, 50, 100, 200, 500, 1000, 1500 $mg \cdot L^{-1}$ Cd $(NO_3)_2$ solution or $Pb(NO_3)_2$ solution containing 0.01$mol \cdot L^{-1}$ $NaNO_3$ as background electrolyte (initial pH 5) .Then each of the solutions was separated using a centrifuge for 10 min at 4000 $r \cdot min^{-1}$ and the supernatant was filtrated by medium filter, of whose Cd or Pb concentration were determined by AAS. All measurements were made in triplicate.

Adsorption experiments of soils with different concentrations of paper sludge: Air-dried soil samples (red soil, purple soil) were weighed 2.000 g in 50 mL polypropylene centrifuge tubes with different percentages paper sludge (0, 0.1%, 0.5%, 1%, 2%, 5%, 10%, 15%). Then added 25 mL Cd $(NO_3)_2$ (500 $mg \cdot L^{-1}$) or $Pb(NO_3)_2$ (800 $mg \cdot L^{-1}$) solution to the centrifuge tubes. The following steps as above.

2.3 Desorption of cadmium and lead

After the separation of soil from the adsorption equilibrium solution in the experiments for adsorption isotherms, 25 mL of 0.01 $mol \cdot L^{-1}$ $NaNO_3$ solutions were added into the centrifuge tube that contains residual soils. After shaking the tubes so hard to make residual soil dispersion, put them on rotary shaker at 200 $r \cdot min^{-1}$ and oscillated them intermittent. Then the samples with solution were separated by centrifuge for 10 min at 4000 $r \cdot min^{-1}$ and the Cd or Pb concentrations of supernatant of samples were analyzed by AAS.

2.4 Statistical analyses

Langmuir equation and Freundlich equation [18] were used to describe the Cd, Pb adsorption by soils and paper sludge. Langmuir equation and Freundlich equation refer to Eq.1, Eq.2.

$$C_e/Q_{ad}=1/Q_mK_L+C_e/Q_m. \quad (1)$$

Where, Q_{ad} is the amount of adsorption ($mg \cdot kg^{-1}$), Ce is the equilibrium concentration of the species in the aqueous solution, ($mol \cdot L^{-1}$), Q_m is the maximum adsorbed metal concentration, K_L is a constant related to the energy of adsorption.

$$InQ_{ad}=InK_F+(1/n)InC_e. \quad (2)$$

Where, K_F and n are the Freundlich constants related to the adsorption capacity and intensity, respectively that determine the curvature and steepness of the isotherm. The K_F constant can give an estimation of the amount of adsorbed metal in $mg \cdot kg^{-1}$ at a solution concentration of 1 $mg \cdot L^{-1}$ [19].

Result and discussion

The characteristics of red soil and purple soil were as follows: pH 6.85, 6.62, organic matter12.83, 36.08 $g \cdot kg^{-1}$, CEC 5.50,14.96 $cmol \cdot kg^{-1}$, Pb 43.26, 44.48 $mg \cdot kg^{-1}$, Cd 0.42, 0.68 $mg \cdot kg^{-1}$, clay 28.7%, 16.2%, silt 51.9%, 53.8%, sand 19.4%, 30.0%.

The characteristics of paper sludge were as follows: pH 7.78, organic matter 198.14 $g \cdot kg^{-1}$, total Nitrogen 1.53 $g \cdot kg^{-1}$, available Nitrogen 170.06 $mg \cdot kg^{-1}$, Total Phosphorus 2.14 $g \cdot kg^{-1}$, CEC 711.15 $cmol \cdot kg^{-1}$, Pb 38.63 $mg \cdot kg^{-1}$, Cd undetected.

3.1 Adsorption characteristics of Cd(Ⅱ) and Pb(Ⅱ)

Adsorption characteristics of Cd(Ⅱ), Pb(Ⅱ) by soils and paper sludge were described by Langmuir and Freundlich equations. The calculated parameters of the equations are provided in Table 1, which showed that both Langmuir and Freundlich equations can fit the data well. All the correlation coefficient (r) of soils are greater than 0.95 (P <0.05).

K_L is an intensity factor in Langmuir equation. The higher values of K_L, The greater ability of bind soil colloids and heavy metal ions [20]. K_L values of the Langmuir equation can be seen from Table 1, the binding capacity of red soil to Cd(Ⅱ) is slightly stronger than purple soil, while that of purple soil to Pb(Ⅱ) is slightly stronger than red soil. In this experiment, MBCs (maximum buffer capacities) of red soil, purple soil for Cd(Ⅱ) are little difference, and MBC values of Pb(Ⅱ) are 355.82 $mg \cdot kg^{-1}$, 1107.15 $mg \cdot kg^{-1}$, MBC values of paper sludge is higher than tested soils. It shows that the MBC of purple soil for Pb(Ⅱ) is greater than red soil, and the MBC of paper sludge for Cd(Ⅱ), Pb(Ⅱ) is greater than tested soils .

Table 1

Parameters of Langmuir and Freundlich equations that were fitted to the Cd(Ⅱ) and Pb(Ⅱ) adsorption data

Heavy metal	Sample	Langmuir				Freimdlich		
		Q_m	K_L	r	MBC	K_F	n	r
Cd	Red soil	2871.34	0.016	0.991	46.80	372.42	0.288	0.967
	Purple soil	4353.69	0.011	0.989	46.58	310.89	0.376	0.991
	Paper sludge	5813.95	0.587	0.996	3412.79	1407.24	1.636	0.992
Pb	Red soil	10914.65	0.033	0.945	355.82	2497.99	0.229	0.995
	Purple soil	14249.07	0.078	0.953	1107.15	2936.01	0.299	0.991
	Paper sludge	17543.86	0.399	0.995	6992.98	4013.87	2.876	0.912

These results show that, adsorption capacity of Pb(Ⅱ) is significantly higher than that of Cd(Ⅱ). For the heavy metal ions of the same valence, adsorption capacities by the same type of soil colloids depend primarily on ions' hydrated ionic radii. So the larger ionic radii, the smaller of their hydrated radius relatively, it's easier to be adsorbed by the surface of the soil colloids under the soil surface gravity [2]. With strong adsorption, ion exchange and expansion abilities, soil clay minerals have good adsorption capacity for major pollutants such as heavy metals and their compounds [21]. Red

soil is mainly developed from the quaternary red clay and Huanggang rocks cane, which composed by 1:1 type clay mineral kaolinite. While purple soil is composed by 2:1 type montmorillonite and illite. 1:1 type clay minerals (kaolinite) consists of a silicon wafer with a tetrahedron octahedral aluminum chips constitute because of a low specific surface area, and there is almost no lattice substituted, therefore it has less negative charge and low content of CEC. 2:1 type clay minerals (montmorillonite, illite) consists of two silicon wafers with an aluminum-oxygen tetrahedron octahedral chip form, substituted by a lattice to produce more negative charge, large expansion, and high content of CEC[22]. So this is one of the reasons for the adsorption of metal ions by purple soil stronger than red soil.

3.2 Desorption characteristics of Cd(Ⅱ) and Pb(Ⅱ)

The results of Cd(Ⅱ) and Pb(Ⅱ) desorption rates by tested soils and paper sludge are presented in Table 2. For Cd, Desorption rate of red soil and purple soil increase with the increase of Cd(Ⅱ) concentration, opposite of paper sludge. The desorption rate of paper sludge reaches maximum (0.23%) at 500 $mg \cdot kg^{-1}$ of Cd(Ⅱ) concentration. Overall, Cd(Ⅱ) desorption rate of paper sludge is lower than tested soils. For Pb, the desorption rate is lower at less than 500$mg \cdot L^{-1}$ of Pb(Ⅱ) concentration, maintained at a basically stable level. Desorption rate increases significantly, and the desorption rate of red soil is greater than purple soil, Pb(Ⅱ) desorption rate has little change as concentration increase higher.

Table2

Desorption ratios of Cd(Ⅱ) and Pb(Ⅱ) on red soil, purple soil and paper sludge (%)

Heavy metal	Soil	Concentration of Cd(Ⅱ) or Pb(Ⅱ) ($mg \cdot L^{-1}$)						
		20	50	100	200	500	1000	1500
Cd	Red soil	0.07	0.13	0.33	2.38	2.25	2.85	3.12
	Purple soil	0.21	0.43	0.64	0.49	0.96	2.00	2.43
	Paper sludge	0.13	0.17	0.16	0.22	0.23	0.07	0.05
Pb	Red soil	0.10	0.20	0.11	0.12	0.11	1.02	1.02
	Purple soil	0.12	0.18	0.09	0.06	0.04	0.27	0.33
	Paper sludge	0.27	0.46	0.28	0.36	0.39	0.36	0.18

3.3 The effect of paper sludge on adsorption of Cd(Ⅱ) and Pb(Ⅱ) by soils

Fig.1 shows that adsorption capacity of Cd(Ⅱ) appears to be a growing trend at percentage of sludge ranging 0-10%, then reaches equilibrium gradually. But Pb(Ⅱ) is faster than Cd(Ⅱ) in this process due to soils adsorbed Pb(Ⅱ) easier than Cd(Ⅱ). Adsorption capacity of Cd(Ⅱ) and Pb(Ⅱ) by purple soil is obvious higher than red soil without paper sludge. After adding paper sludge, the adsorption capacities of Cd(Ⅱ) increase by 49%,25%, and by 22%,30% of Pb(Ⅱ). This may be due to the sludge's addition changes the physical and chemical properties of tested soils, particularly paper sludge organic matter, CEC. Organic matter content of paper sludge is almost 15, 5.5 times that of red soil, purple soil respectively, and 129.3, 47.7 times of CEC. Many studies had showed that organic matter, CEC content were two important factors that affect the adsorption of heavy metals in soil [23].

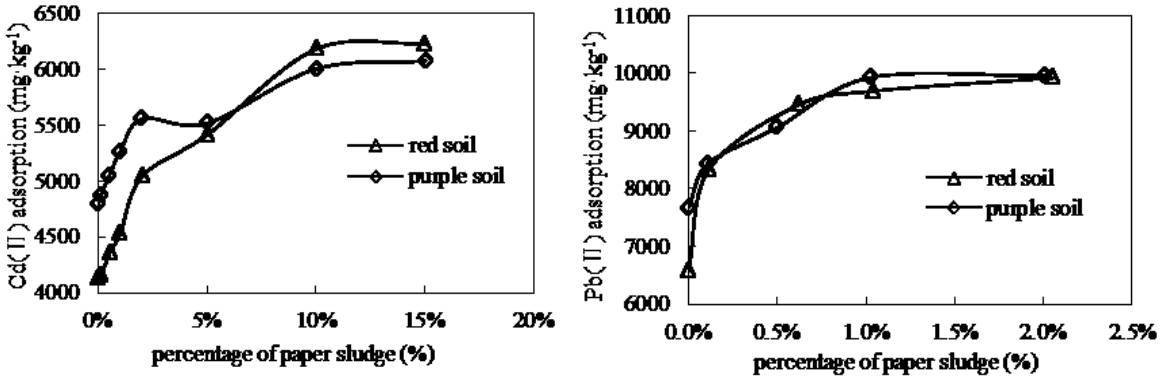

Fig.1 Adsorption isotherms of Cd(Ⅱ) and Pb(Ⅱ) in red soil, purple soil on different percentages of paper sludge

Organic matter and CEC play important role in the soil for heavy metal adsorption reaction. The effect of organic matter may be explained as follows. Humus contains a lot of oxygen containing functional groups, such as carboxyl, phenolic hydroxyl, alcoholic hydroxyl, and they are easy to react with heavy metal by complexation and chelation. Thereby heavy metal ions are fixed and hard to desorbed [19].

The organic matter content of paper sludge in research is up to 198.14 mg·kg^{-1}. Paper sludge addition improves the concentration of organic matter in soils, and enhance the lag effect, so that Cd (Ⅱ) and Pb(Ⅱ) adsorption by soils increase and become irreversible [24]. CEC reflects the negative charge amount of soil colloids, higher of CEC, the higher amount of negative charge, it can provides more adsorption points to adsorb heavy metal ions in order to increase the amount of adsorption of heavy metals by soils[25]. Cd(Ⅱ) adsorption on iron and aluminum oxides and silicates level is controlled by CEC [16]. Cd(Ⅱ) adsorption is positively correlated with CEC. The CEC content of paper sludge in research is up to 711.2 cmol·kg^{-1}. Paper sludge addition improved the soil's CEC concentration.

3.4 Effect of paper sludge on Cd(Ⅱ) and Pb(Ⅱ) desorption by soils

Desorption capacities of Cd(Ⅱ) by red soil and purple soil are 215.5 mg·kg^{-1}, 190.6 mg·kg^{-1}, without paper sludge addition. Desorption of Cd(Ⅱ) reduce gradually with the increase of ratio of paper sludge addition, then reach the lowest points at 1.0 mg·kg^{-1} (red soil), 0.08 mg·kg^{-1} (purple soil) when sludge ratio is 5%. When the sludge is greater than 5%, desorption rebounded but remain low and maintained at 10 mg·kg^{-1} or less. Desorption capacities of Pb(Ⅱ) by red soil and purple soil are 76.3 mg·kg^{-1}, 34.1 mg·kg^{-1} without paper sludge addition. When the sludge addition is 2%, desorption capacities reach lowest, which were 2.21 mg·kg^{-1} (red soil), 0.06 mg·kg^{-1} (purple soil), then remain low. While Fig.2 shows that, desorption declined rapidly, when added by paper sludge 0.1%. Which may be depend on the desorption of Pb(Ⅱ) by tested soil is less than Cd(Ⅱ). It is more obvious for same amount of paper sludge influence on Pb(Ⅱ) desorption.

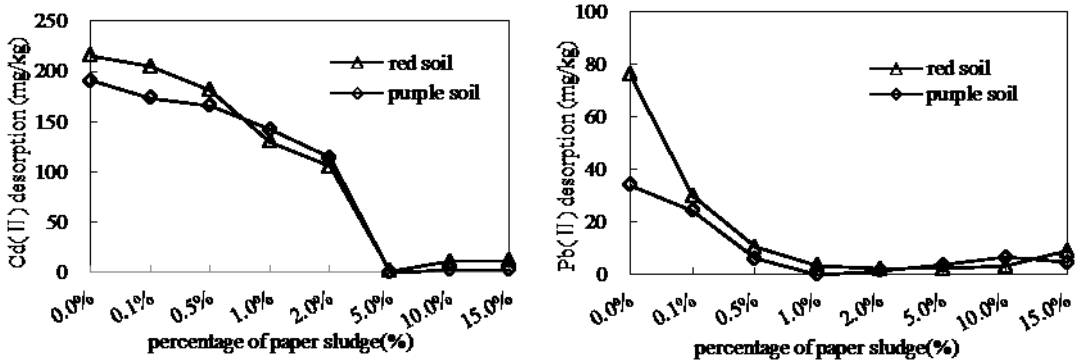

Fig.2 Desorption isotherms of Cd^{2+} and Pb^{2+} in red soil, purple soil on different percentages of paper sludge

Conclusions

This study shows that Cd(Ⅱ) and Pb(Ⅱ) adsorption can described by Langmuir equation and Freundlich equation well. Adsorption of Cd(Ⅱ) and Pb(Ⅱ) by purple soil is higher than red soil, but opposite of desorption. Freundlich equation is used to fit the adsorption data of paper sludge better than Langmuir equation, and the adsorption capacity is greater than tested soils, while desorption capacity is less than the tested soils. With the same concentration of heavy metal, addition of paper sludge improve Cd(Ⅱ) adsorption capacities by 49%(red soil), 25%(purple soil), and Pb(Ⅱ) adsorption capacities by 22%, 30%, respectively. And decreased Cd(Ⅱ) desorption by 99.5%, 99.9%(at lowest point of desorption), Pb(Ⅱ) desorption by 97.5%,99.8%, respectively. Paper sludge effectively enhance the adsorption capacities of the tested soils and capabilities of fixed Cd(Ⅱ), Pb(Ⅱ).

Paper sludge land application can not only ease the migration of heavy metal in soil-crop systems, but also provid conditions for the utilization of paper sludge. Though paper Sludge can reduce the effectiveness of heavy metals to some extent, more studies are needed to research whether paper sludge can prevent migration of heavy metals in soil-crop system or not, especially reduce the concentration of heavy metal in some edible agricultural products to meet safety standards.

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