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Competitive adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+} onto Fe^{3+}-modified argillaceous limestone: Influence of pH, ionic strength and natural organic matters

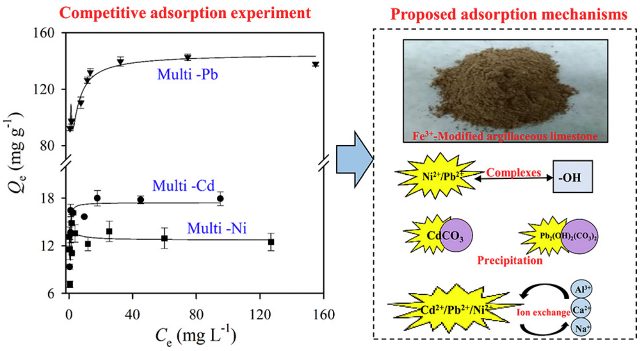
Shuran He [a], Yongtao Li [a,c], Liping Weng [c], Jinjin Wang [a], Jinxian He [b], Yonglin Liu [a], Kun Zhang [a], Qihong Wu [a], Yulong Zhang [a,*], Zhen Zhang [a,*]

[a] *College of Natural Resources and Environment, Joint Institute for Environmental Research & Education, South China Agricultural University, Guangzhou 510642, China*
[b] *School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, China*
[c] *Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China*

HIGHLIGHTS

- Fe^{3+}-modified argillaceous limestone showed effective adsorption of Cd^{2+}/Pb^{2+}/Ni^{2+}.
- The adsorption selectivity of the metals followed the order of Pb ≫ Cd > Ni.
- Both pH and ionic strength played key roles in metal adsorption.
- Humic acid and glycine exerted distinct effects on adsorption behaviors of metals.
- Mechanisms of metal adsorption were ion exchange, precipitation and complexation.

GRAPHICAL ABSTRACT



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ABSTRACT

In present study, the feasibility of applying a natural adsorbent with Fe^{3+} modification (Fe^{3+}-modified argillaceous limestone, FAL) on the competitive adsorption of heavy metals (i.e., Cd^{2+}, Pb^{2+} and Ni^{2+}) was evaluated. The current results revealed an efficient adsorption on Cd^{2+}, Pb^{2+} and Ni^{2+} in mono-metal system. Further experiments demonstrated a high selectivity of Pb^{2+} during the competitive adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+}. The adsorption selectivity of the metal ions followed the order of Pb ≫ Cd > Ni. In addition, both pH and ionic strength are important factors affecting the metal adsorptions. It is interestingly that various NOMs (i.e., humic acid (HA) and glycine (Gly)) exerted different effects on the adsorption behaviors, probably due to the different affinities for Pb^{2+}, Cd^{2+} and Ni^{2+} and the redistribution of newly-formed metal-DOM complexes. X-ray photoelectron spectroscopy (XPS) analysis together with X-ray diffraction (XRD) and energy dispersive spectrometer (EDS) analysis revealed that the metal adsorptions were mainly regulated via the synergistic mechanisms of ion exchange by Na^{+}, Ca^{2+}, and Al^{3+}, precipitation to form $CdCO_3$ and $Pb_2(OH)_2(CO_3)_2$, as well as complexes of FAL-OPb and FAL-ONi by hydroxyl groups on the surface of FAL. The application of FAL would be a promising option in leading to an efficient heavy metal removal.

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* Corresponding authors.
E-mail addresses: yongtao@scau.edu.cn (Y. Li), wengliping@caas.cn liping.weng@wur.nl (L. Weng), wangjinjin@scau.edu.cn (J. Wang), jxhe@cumt.edu.cn (J. He), yulongzhang@scau.edu.cn (Y. Zhang), zzhangal@scau.edu.cn (Z. Zhang).

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1. Introduction

In recent years, increasing amounts of heavy metals are produced from many industries such as mining, ore refining, batteries and alloy manufacturing and their release into environment has raised a great public concern. Cd, Pb and Ni have been listed as priority pollutants by the US Environmental Protection Agency (EPA) because of their distinct toxicity, potential carcinogenicity, persistent properties, as well as high bioaccumulation tendency (Bourliva et al., 2015; Li et al., 2009b). Furthermore, different heavy metals normally coexist in wastewater and contaminated soil and lead to an increased detriment to organisms (Wang et al., 2013). Therefore, it is of great necessity to explore proper approaches that can effectively remove heavy metals such as Cd, Pb and Ni from not only single but also ternary aqueous solutions.

Heavy metals can be removed from aqueous solutions through several ways including chemical precipitation, electrolytic process, ion exchange, membrane filtration and adsorption(Fu and Wang, 2011). Among these methods, the adsorption has been considered as a promising method since this technique is normally easy to operate and cost-effective for the removal of heavy metal even at low concentrations (Fu and Wang, 2011). Obviously, selecting a proper and effective adsorbent become of specific importance in order to guarantee a satisfactory performance of heavy metal removal. Many studies focused on employing synthetic adsorbent and generally achieved a satisfactory performance for heavy metals removal (Tang et al., 2012; Wang et al., 2011). But excessive use of synthetic adsorbents has inevitably brought a series of potential environmental concern (Chow et al., 2005). Padrova et al. (2016) have reported that two of the commercial synthetic adsorbents (i.e., Nanofer 25 and Nanofer 25S) are toxic to the soil microorganisms. As a result, natural adsorbents, which are naturally formed or retrieved from the natural materials with insignificant risks to the environment, have again attracted the researchers' attention in recent years due to its low-cost and non-invasive properties (Bourliva et al., 2015).

Argillaceous rocks are one of the most widely distributed type of sedimentary rock. In the category of argillaceous rocks, argillaceous limestone normally exists together with grey limestone in the environment (Zagrarni et al., 2008). For centuries, grey limestones have been widely used as the source of building materials. On the contrary, argillaceous limestone nowadays still received less attention since relatively low amount of carbonate component in argillaceous limestone limited its usage in the construction field. However, both the carbonate mineral and the clay mineral in argillaceous limestone are considered to be beneficial for heavy metal removal due to the potential to precipitate heavy metals by carbonate minerals (Sipos et al., 2008) and the high cation exchange capacity of the clay mineral (Uddin, 2017). Besides, after mining the grey limestones, large amount of argillaceous limestone is exposed in the mining area without any further usage. Thus, the abundance and availability of these argillaceous limestones make them a potential candidate to be a low-cost natural adsorbent. Considering above properties of argillaceous limestone, it becomes of interest if the heavy metal ions such as Cd^{2+}, Pb^{2+} and Ni^{2+} could be effectively adsorbed by argillaceous limestone. However, such information on the feasibility of applying argillaceous limestone in heavy metal removal is sorely lacking. And an investigation on the adsorption behaviors of Cd^{2+}, Pb^{2+} and Ni^{2+} to argillaceous limestone in the mono-metal or multi-metal systems is still needed. Introducing inorganic salt such as ferric salt has been reported to be one of the efficient methods for adsorbent modification. For example, iron oxides have high affinity for metals due to their large surface area, microporous structure and internal surface (Dimirkou and Doula, 2008). However, little information is available yet on the removal of Cd^{2+}, Pb^{2+} and Ni^{2+} using argillaceous limestone modified with $Fe(NO_3)_3$ and how the environmental factors, such as pH, ionic strength and natural organic matter (NOM), influence the removal process.

Nevertheless, it is generally accepted that the presence of NOM may exert a significant influence on heavy metal removal by adsorbent (Tang et al., 2014). However, most of the previous studies were still limited to only one type of NOM (Wang et al., 2013), and study on the adsorption of heavy metals onto argillaceous limestone in the presence of different NOMs remains sparse. Therefore, the objectives of this study were (i) to characterize the Fe^{3+}-modified argillaceous limestone (FAL) and to evaluate its adsorption kinetics and adsorption capacity for Cd^{2+}, Pb^{2+} and Ni^{2+} in mono-metal or multi-metal systems; (ii) to investigate the effects of environmental conditions including pH, ionic strength and species on Cd^{2+}, Pb^{2+} and Ni^{2+} adsorptions by FAL; (iii) to explore the interaction between FAL and heavy metals (i.e., Cd^{2+}, Pb^{2+} and Ni^{2+}) in the presence of a high-molecular-weight NOM (i.e., HA) and a low-molecular-weight NOM (i.e., Gly); and (iv) to elucidate the mechanisms involved in adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+} by FAL. It is expected that the outcomes from the study could provide understanding for the application of FAL as a low-cost natural adsorbent for heavy metal removal.

2. Materials and methods

2.1. Materials and chemicals

The raw mineral material was sampled from the lower Cambrian Mantou Fm in Dabeiwang area in Jiangsu Province. In this area, mixed sedimentation of carbonates and terrigenous clastics is a commonly found sedimentary phenomenon. The geochemical characteristics of this raw mineral material are shown in Table A.1. It can be seen that the major components of the raw mineral material are carbonate minerals. In addition, the proportion of clay mineral is around 12.2% (Table A.1). Based on the proportions of carbonate mineral and clay mineral, the raw material used in current study can be roughly classified as argillaceous limestone.

Sodium chloride (NaCl), sodium nitrite ($NaNO_3$), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), nitric acid (HNO_3, 70% (w/w)), sodium hydroxide (NaOH) of analytical grade, iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 99.99%), lead nitrate ($Pb(NO_3)_2$, 99.99%), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99.99%), cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2O$, 99.99%) and Gly ($C_2H_5NO_2$, 99.9%) were purchased from Aladdin Reagent Database Inc. (Shanghai, PR China). HA was purchased from Sigma-Aldrich (MO, USA).

2.2. Modification of argillaceous limestone

The FAL was synthesized according to the previous method described by Doula (2006). Specifically, 20.0 g of raw argillaceous limestone (RAL) pretreated by grinding was mixed with 100 mL of freshly prepared $Fe(NO_3)_3 \cdot 9H_2O$ solution (1 M) and 180 mL of NaOH solution (2 M) under intense agitation in a 2-L Teflon flask. The suspension was diluted to 2 L with twice-distilled water and was held in a closed Teflon® flask at 80 °C for 48 h. Afterwards, the precipitate was centrifuged at 4000 rpm for 5 min, then washed until free of NO_3^- ions and finally air dried at room temperature.

2.3. Adsorption experiment

In this experiment, 1000 mg L^{-1} Cd^{2+}, Pb^{2+} and Ni^{2+} were prepared by dissolving specific amounts of $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$, and $Ni(NO_3)_2 \cdot 6H_2O$ in deionized (DI) water. All the experiments were performed with three replicates. 0.0075 g of FAL adsorbents was added into 50 mL-solution (final concentration 0.15 g FAL/L) with varying initial concentrations of Cd^{2+}, Pb^{2+} and Ni^{2+} (1–200 mg L^{-1}). The initial pH values of the suspensions were adjusted using 0.1 M HNO_3 or NaOH until the desired pH was reached. The suspensions were placed in a thermostatic steam bath vibrator (HS-211C, HASUC, China) at a speed of 180 rpm at 25 °C for 720 min. Time duration of 720 min was chosen based on our preliminary study (see the Supporting Information (SI) (Appendix B)). Afterward, the particles and the aqueous phase were separated by centrifugation at 8000 rpm for 3 min. The supernatant were filtered through a 0.22-μm membrane filter and