Competitive sorption of lead and methylene blue onto black soil and their interaction with dissolved organic matter using two-dimensional correlation analyses

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ABSTRACT

This study investigated the competitive sorption of black soil to adsorb Pb(II) and methylene blue (MB) from multi-contaminated soils. According to the experimental data, the process of adsorption can be clearly explained by pseudo-second-order kinetic equation. Both single and binary systems of the adsorption isotherms had a good fit with Langmuir models. The maximal adsorption abilities of Pb(II) and MB acquired from binary systems sorption were attenuated compared to those from the single system (Pb(II): $77.70 > 65.96 \, \mathrm{mg \, g^{-1}}$; MB: $242.31 > 222.36 \, \mathrm{mg \, g^{-1}}$). Pb(II) and MB can inhibit each other's sorption ability. A combination of three-dimensional excitation-emission matrix (3D-EEM), synchronous fluorescence spectra as well as two-dimensional correlation spectroscopy (2D-COS) were employed to determine the binding of dissolved organic matter (DOM) for Pb(II) and MB during soil sorption process. As a result, 3D-EEM implicated that the two main composes of DOM were humic acid-like substances and the fluorescence of DOM specimens were gradually diminished with increasing concentrations of Pb(II) and MB. According to synchronous fluorescence spectra, static quenching of Pb(II) and MB mainly led to fluorescence quenching. Specifically, fluorescence-2D-COS implicated that Pb(II) and MB bound to fluorescence in the following sequence: the earlier occurrence of the humic-like fraction compared to that of protein-like fraction. FTIR-2D-COS results concluded that the structural change sequence of DOM by Pb(II) binding followed the order: $1700 > 863 > 1332 > 1529 > 1200 > 1086 \, \mathrm{cm^{-1}}$ and the sequence of the MB binding affinities followed the order: $1520 > 1399 > 1345 > 1152 > 1602 > 993 > 881 \, \mathrm{cm^{-1}}$. These findings would be beneficial to understand the mechanism of adsorb multi-component systems and have the potential to contribute significance to the interaction mechanism of multi-component with soil DOM at the molecular level.

1. Introduction

The black soil zone of the northeast China is among the three largest mollisol regions globally. Particularly, black soils play an essential role in the maintenance of food security among all soil resources in China. Due to purity of black soil as agricultural land containing adequate organic matter, it also harbors superior physical and chemical features (Zhang et al., 2015). In recent years, there has been a significant degeneration of black soil, the major problems are soil fertility deterioration and soil contamination (Xu et al., 2010; Fang et al., 2012). Industrial, agricultural, garbage and other pollution can exert great destruction on soil environment in consideration of their toxicological nature, posing a great threat to human health and ecological safety (Fang et al., 2017).

Large quantities of typical inorganic and organic toxic compounds,

such as heavy metals and dyes, also exist in wastewater from diverse industries, and pollutants can migrate with water into the soil (Körbahti et al., 2011). Soil adsorption is an extremely important behavior of pollutants in the natural environment, which controls the transfer, accumulation, activity and degradation of pollutants. The adsorption isotherm is the most important way to explore the adsorption process (Langmuir, 1916). However, most of the studies are aimed at single pollutant, on which, many scholars have carried out deep research. Lin et al. (2017) reported that the adsorption-desorption characteristics of atrazine in three soils were evaluated, indicating that atrazine in soils was completed in two steps and could be clearly explained by pseudo-second-order mode. ln addition, Freundlich and Langmuir models were well fitted to the nonlinear adsorption isotherms. Divisekara et al. (2018) researched the effect of a commercial glyphosate formulation on adsorption of heavy metal ions on paddy soil, implying that at low

initial concentrations of metal ion, Langmuir adsorption isotherm model is followed, while at concentrations, Freundlich adsorption isotherm model is followed, with or without glyphosate. However, till now, there are limited reports focusing on the competitive adsorption of multi-component situations exist in soil environmental system.

Soil, a heterogeneous and complicated material system, functions as a first prevention line against the groundwater contamination via partial adsorption of toxic substances (Safruk et al., 2017; Wang et al., 2017). Dissolved organic matter (DOM) has been prevalently shown to be critically involved in biochemistry cycling of environmental contaminants (Xia et al., 2013, 2015). DOM is considered as a main soluble constitute of natural aquatic and soil systems, which is critically involved in the environmental fate of diverse contaminants in multiple ecological functions (Sakellariadou, 2016). The following reasons can be used to illustrate the importance of DOM in soil: (1) DOM decreases or even eliminates the compaction of soil; (2) DOM provides adequate nutrients for soil organism and plant growth; (3) In addition, DOM attenuates the negative influence of pesticides, heavy metals, and other kinds of environmental pollutants (Park et al., 2009). Therefore, it is important to explore the mechanism as well as interaction of DOM with one single component existing in multi-component conditions as well.

There are various studying approaches for identification of the properties of pollutants binding with DOM, including fourier transform infrared spectroscopy (FTIR), size exclusion chromatography, differential absorbance titration, scanning electron microscopy (SEM) as well as equilibrium dialysis (Michael et al., 2015). Fluorescence spectroscopy, with rapid and satisfactory selectivity as well as high sensitivity, has been prevalently utilized for identification of DOM. Zhu et al. (2018) reported that four types of land DOM from soils under were employed for exploration of the binding features of atrazine, which showed DOM from different sources harbored diverse structures, and humic-like components exhibited more significant quenching effects in comparison to protein-like components. Hur and Lee (2011) demonstrated that copper could quench hydrophobic acid and hydrophilic fractions of DOM, implicating a better heavy metal binding capacity of DOM. In studies performed by Magner et al. (2009) and Yamamoto et al. (2003) reverse-phase separation and dialysis were used for characterization of the binding of endocrine disruptors, insecticides and fungicides to DOM, respectively. Nevertheless, limited data have been accessible to probe into the binding mechanism between DOM and multi-component situations. To this end, it is of great importance to establish an efficient approach to explore and elucidate the mechanism in multi-component simultaneous sorption process.

Regarding that metal pollution could exert a simultaneous effect on multiple pollutants, it is intriguing to research multi-component systems. Hence, the study was designed to evaluate the sorption and interaction mechanism of simultaneous distribution of multi-component systems onto black soil. To achieve this purpose, Pb(II) and MB were employed as a typical heavy metal ion and organic compounds, respectively. We utilized single and binary systems for investigation of the simultaneous adsorption process, as well as for identification of the sorption kinetics and isotherm. In addition, three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy and synchronous fluorescence technology were used for analysis of the physical properties, chemical composition, as well as concentration and distribution of DOM specimens after Pb(II) and MB addition. 2D-COS was used to clarify the dynamic molecular variations of organic ligands, as well as to enhance the spectral resolution. All in all, our outcomes were quite beneficial, offering valuable information for a comprehensive understanding to investigate the behavior of multi-component contaminants sorption onto black soil, which also supplied a theoretical basis for preventing and managing black soil pollution.

2. Materials and methods

2.1. Reagents and materials

Chemicals, MB ($C_{16}H_{18}N_3SCl$, MW 373.90) and lead nitrate (Pb(NO_3)$_2$, 99.0%), were obtained from BASF Chemical Reagent Tianjin Co., Ltd., All other chemical reagents used in the experiments were analytical reagent grade. The solutions were prepared with ultrapure water (EASY-pure LF, Barnstead International, Dubuque, Iowa USA).

Soil specimens at depth of 0–20 cm (surface soil) were collected from the black soil zone, Xiangfang Experimental Farm, Harbin, Heilongjiang Province, China (126°43′16″E, 45°44′23″N), followed by drying in air, removal of stones and visible roots, fauna and subsequent sieve via a mesh of 2 mm. Besides, no residual Pb(II) and MB was found in soil specimens.

2.2. Extraction of soil DOM

In the extraction of DOM, 20 g of soil was added into 250 mL conical flask, which contained 200 mL distilled (DI) water and 0.01 mol L^{-1} $CaCl_2$, followed by shaking at 125 rpm at 25 °C for 24 h (Wang et al., 2017). After centrifuging at 5000 rpm for 10 min, and filtrating through a 0.45 μm membrane filter, the suspension was collected (Fu et al., 2016; Jiang et al., 2017). The filtrates were reserved at dark at 4 °C until used for preparation of fluorescence quenching titration.

2.3. Preparation of Lead and MB stock solution

Pb(NO_3)$_2$ was dissolved into de-ionized water to acquire the stock solution with 1000 mg L^{-1} Pb(II). Accurate amount MB as dissolved in deionized water to prepare the MB stock solutions at a concentration of 1000 mg L^{-1}. $CaCl_2$ (0.01 M) was utilized for stimulation of the background electrolytes of soil solution and 0.02% NaN_3 was employed for suppression of microbial activity (Wang et al., 2009). The concentrations of both dye ions and metal ions prepared from stock solutions ranged from 50 mg L^{-1} to 500 mg L^{-1}. In terms of binary metal-dye solutions, dilution of 1000 mg L^{-1} of stock solutions of metal ions and dye ions and subsequent mixture in the test medium were performed to obtain desired combinations of Pb(II)-MB ions. Before mixing with black soil, the initial pH value was modified to 6.0 by addition of NaOH or HCl solutions (0.1 mol L^{-1}) (Shi et al., 2015).

2.4. Batch sorption experiment

The sorption kinetic experiments in single and binary sorption systems were performed at room temperature (25 °C). In single sorption system experiment, about 0.2 g of black soil was added to 100 mL of Pb(II) or MB solutions with diverse initial concentrations (50, 100, 250 mg L^{-1} for Pb(II) and MB). The effect of contact time was performed at specific time points of 0–360 min with Pb(II) or MB solutions of diverse initial concentrations. In terms of binary sorption system experiment, the mixture of Pb(II) and MB created a solution containing 150 mg L^{-1} Pb(II) and 150 mg L^{-1} MB, followed by addition of 0.2 g of black soil and subsequent stirring at 200 rpm for 0–360 min.

For adsorption isotherm experiment, we added 0.2 g soil into 100 mL conical flask, which contained diverse concentrations of Pb(II) or MB (50–500 mg L^{-1}). In terms of binary systems, the concentration ratio of metal-dye mixed solution was constantly fixed at 1:1 (v/v) from 50 to 500 mg L^{-1}, followed by stirring for sorption equilibrium.

The removal efficiency onto adsorbent and the adsorption amount q_t (mg g^{-1}) at different time of Pb(II) or MB were generated by the following Eqs. (1) and (2) (Lin et al., 2017):

$$Removal\,efficiency(\%) = \frac{(C0 - Ct)}{C0} \times 100\% \quad (1)$$