Equilibrium, kinetic and thermodynamic studies of Pb(II) adsorption from aqueous solutions on HCl-treated Egyptian kaolin

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A B S T R A C T

HCl activated (HK) and untreated (UnK) Egyptian (Sinai) kaolin were characterized. The adsorption parameters of Pb(II) on UnK and HK were examined in aqueous solutions. The equilibrium adsorption data were described using Langmuir and Freundlich adsorption isotherm models. The monolayer adsorption capacities were 34.5 and 23.8 mg g^{-1} at pH 5.5 and 25 °C for the HK and UnK, respectively. The experimental data fitted well the pseudo-second-order kinetics model. The thermodynamic parameters standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy changes ($\Delta S°$) for the adsorption process were calculated. The negative value of the Gibbs free energy confirms that the adsorption processes are spontaneous and thermodynamically favorable while the positive value of $\Delta H°$ supports the endothermic physical adsorption process. HK was applied successfully for removing Pb(II) (67.5–99.3%) from spiked water samples and >98% of the loaded Pb(II) ions was recovered by 1 mol L^{-1} HNO$_3$. The successful removal of Pb(II) from the studied water samples indicates that HK can be used efficiently for pollution remediation of fresh water from lead.

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1. Introduction

Water pollution is of major concern for human health as well as for the environmental quality. Heavy metals represent a category of toxic substances that are the most dangerous for the environment. Lead is considered among the most toxic elements of the heavy metals, as it is not biodegradable and thus considered as a risk factor for human health. Its extensive use worldwide, in the past, was attributable to its extraction facility, malleability and low melting point [1,2]. It has been used for different purposes such as water pipes, glassware, paints, ceramics, fuel additives and batteries. According to the World Health Organization (WHO), the maximum tolerable concentration of lead in water for human use is limited to less than 10 mg L^{-1} [3]. Therefore, the removal of Pb(II) from effluents is fundamental for pollution remediation.

Different methods for removing Pb(II) ions from aqueous solutions have been documented including biosorption [4], ion exchange [5], elctrodialysis [6] and ultra filtration membrane separation [7,8]. Such methods are either expensive, time consuming and/or wasteful, particularly when the concentrations of heavy metal ions are more than 10 mg L^{-1}.

On the other hand, the adsorption process of Pb(II) is an appropriate, economic and reasonably workable technique for removing heavy metal ions especially when the adsorbent is easily regenerated [9–12]. In this regard, researchers have reported the use of different cheap adsorbents such as agricultural and industrial wastes [10,11] and zeolite [12].

Raw and modified clays are also utilized as adsorbent materials for removing heavy metals [13–16]. The unique hydrophilic surface properties of clays such as bentonite and kaolin, gave them exceptional adsorbent capabilities that might be increased by various treatments.

Kaolinite, a layered silicate mineral having Al$_2$Si$_2$O$_5$(OH)$_4$ formula, is the main constituent of kaolin. It is characterized by a relatively small surface area, commonly ranging from 10 to 20 m^2 g^{-1}, and the least exchangeability (15–75 μmol g^{-1}) among other clay minerals [17–24]. It is rather preferred for its low cost and wide abundance.

The particular potential of kaolin for the adsorption of metal ions including Pb(II) from solutions have been confirmed, and

thoroughly described using the equilibrium isotherms; linear Langmuir and Freundlich models with preference to the latter model. It was reported that the removal of Pb(II) by kaolin is based on adsorption as well as ion exchange mechanisms [16–20]. Miranda-Trevino and Coles [19] referred to the decrease of pH during the adsorption of Pb(II) on kaolinite, which indicates the release of H^+ by the mineral, probably involving the hydroxyl edge sites and exposed hydroxyl planes during the adsorption process. Thermodynamic parameters, free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) showed that the adsorption of Pb(II) on natural kaolin was feasible, spontaneous and exothermic process in nature [17,22]. On the other hand, Unuabonah et al. [21,22] reported that the adsorption process is endothermic, which may be related to the dissimilarity in composition and formation origin of the used kaolin. The kinetic studies of Pb(II) adsorption on kaolin have been also reported, it showed that process adopts pseudo-second-order kinetics [17,21]. The unique hydrophilic surface properties of clays such as bentonite and kaolin gave them exceptional adsorbent capability; furthermore this capacity as well as selectivity could be enhanced upon specific treatments. Intercalation, pillaring, and other chemical treatments represent the most common techniques used in this scope [14,16,21–26]. For instances, orthophosphate [21], tri-polyphosphate [23], tetraborate [25] polyvinyl-clay surface, [24] zero-valent iron [26], and ZrO-modified [13,16] have been used in the modification of kaolin.

Large commercial reserves of kaolin deposits exist in Egypt in three major areas namely, Sinai, Red Sea and Aswan [27–30]. Deposits from Upper Egypt were used successfully for the removal of heavy metal ions including Pb(II) [31]. Raw kaolin has also been used for removing Pb(II) from water samples [16,18,22]. Although HCl has been often used for the activation of silanol groups on silica and clay surfaces, to the best of our knowledge no information is yet available on the removal of Pb(II) on HCl-activated kaolin. The aim of the present work is to assess the physico-chemical and adsorption potential characteristics of untreated and HCl-treated Sinai kaolin, as a low cost adsorbent, for removing Pb(II) ions from aqueous samples.

2. Experimental

2.1. Materials

The raw kaolin samples were collected from the deposit of the early cretaceous age exposed at Wadi El Hamadiya area, western scarp of El Tih plateau, South Sinai, Egypt. It belongs to the Malha formation that is mainly formed of kaolinite mineral (89% in average) together with quartz as a non clay mineral [28]. All the used chemicals and reagents were of highest purity grade from Sigma–Aldrich. For application, the water samples; tap water (A and B), Nile River, Lake Manzalah and shrimp fishery were obtained from Giza, Mansoura, El-Matariyah, and Fayoum, respectively, in Egypt. The water samples were filtered and used as it is.

2.2. Equipment

The kaolin samples were subjected to powder X-ray diffraction (XRD) analysis to determine their mineralogical composition using Cu Kα radiation and a Ni filter at constant voltage 40 kV, and 30 mA using Empyrean Powder Diffractometer. Chemical analyses for the major oxides (wt%) and some minor elements of the raw kaolin and the refined treated samples have been performed using X-ray fluorescence spectrometry (XRF) on a modern wavelength dispersive spectrometer (Axios, WD-XRF Spectrometer, PANalytical, 2005, Netherlands). Thermogravimetric analysis (TGA) was performed on a SDT Q600 (TA Instruments, USA) thermal analyzer

at a heating rate of $10\,°C\,min^{-1}$ under nitrogen. Scanning electron microscope (SEM) images were performed on JXA 840A electron probe microanalyzer, Japan. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS10, Thermo-Fisher Scientific, USA, using KBr pellet. Specific surface area (S_{BET}) was determined with a BELSORP-mini II, BEL Japan, INC, using nitrogen at 77 K. S_{BET} was determined following the BET-Method [32]. The residual concentration of Pb(II) was determined using APHA 2005 standard method on a Varian 220 flame atomic absorption spectrophotometer (FAAS). For each series of measurements, absorption calibration curve was constructed of a blank and three or more standards. A standard reference material for Pb(II) in water and quality control sample from National Institute Standard and Technology (NIST, USA) UN 3264HC 077866 from Merck, were used to confirm the instrumental metal concentration readings. Instrumental detection limit for lead was $0.01\,mg\,L^{-1}$. The pH of the solution of each sample was adjusted with NaOH and HNO_3 solutions, using a Hanna Instruments, 8519, Italy, pH/mV meter with an expanded scale and having an accuracy of ±0.1. The pH-metric titration measurement was performed using a Metrohm automatic potentiometer 848 Titrino. An amount (200 mg) of the investigated sample was added to 50 mL of $4.4 \times 10^{-3}\,mol\,L^{-1}$ HCl + $0.13\,mol\,L^{-1}$ KCl and titrated against $7.6\,mol\,L^{-1}$ KOH + $0.25\,mol\,L^{-1}$ KCl at 25 °C with a titration rate $4.2\,mL\,min^{-1}$.

2.3. Methodology

2.3.1. Kaolin treatment

A composite sample (6 kg) was prepared by mixing the collected channel samples from the total thickness of the kaolin beds, along the exposed faces. The prepared sample was crushed, dried at 110 °C for 1 h, ball-milled and named raw kaolin. Then, it was sieved to −112 μm and the obtained fraction (about 50% of raw kaolin) represented the untreated kaolin (UnK). Finally, 100 g of UnK was refluxed at 80 °C in 150 mL HCl ($5\,mol\,L^{-1}$) for 1 h [33], filtered, washed with distilled water, dried at 70 °C for 5 h, and named HCl-treated sample (HK) [34].

2.3.2. Adsorption studies of Pb(II) ions

The adsorption experiments were carried out at room temperature of 25 ± 2 °C. To investigate the effect of pH on the adsorption behavior of lead ions, 50 mL volume of $100\,mg\,L^{-1}$ Pb(II) as nitrate was added individually to 0.1 g of the treated kaolin (HK). The resulting solutions containing adsorbent were agitated for 2 h. The pH values (2.5, 4.5, 5.5, 6.5 and 8.5) were controlled throughout the experiment using 0.1 M NaOH and HNO_3 solutions. The suspensions were filtered and the residual concentration of lead ions in solution was determined by FAAS. The thermodynamic studies of the adsorption of Pb ions on the treated kaolin was studied at three different temperatures (25, 40 and 60 °C) by adding 0.1 g of the adsorbent to 50 mL of the metal ion solution at initial concentration of $100\,mg\,L^{-1}$ and pH of 5.5 for 2 h.

For the effect of dosage studies, the initial pH value of 50 mL $100\,mg\,L^{-1}$ Pb(II) was adjusted at 5.5 and shaken with 0.05–0.5 g HK for 2 h. The final concentration of unadsorbed lead ions was then determined.

For equilibrium studies, only the initial pH value of the metal solution was controlled upon adding UnK or HK. A 0.1 g of dried sample was added into 50 mL of initial concentrations of 10, 20, 50, 100 and $150\,mg\,L^{-1}$ of lead ion solutions in a 250 mL stopper conical flasks under shaking for 24 h. The final concentration of residual lead ions was determined as mentioned before.

For metal-removal kinetics studies, 1 g of HK was vigorously agitated with 500 mL of metal solutions at initial Pb(II) concentrations of 50, 100 and $150\,mg\,L^{-1}$ in a beaker using a magnetic stirrer at a constant temperature of 25 °C. In all cases, the pH was