Applied Clay Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

# Effect of ball milling process on the structure of local clay and its adsorption performance for Ni(II) removal

Shahrzad Maleki, Ayoub Karimi-Jashni *

*Department of Civil and Environmental Engineering, Shiraz University, Po. Box 7134851156, Shiraz, Iran*

ARTICLE INFO

*Article history:*
Received 19 March 2016
Received in revised form 23 October 2016
Accepted 5 December 2016
Available online xxxx

*Keywords:*
Ball milling
Natural clay
Ni(II) removal
Isotherm
Kinetics

ABSTRACT

The effect of ball milling process on the properties of the natural local clay including structural changes and adsorption capacity for the removal of Ni(II) ions from aqueous solutions, was investigated. The local clay was ground at varying times from 5 to 20 h with a 10:1 or 20:1 weight ratio of the balls to powder, which produced six different ball milled clays (BM-Clay1 to BM-Clay6). Ground clays were then characterized by particle size measurement, X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy analysis, and adsorption experiments. These analyses were performed to evaluate the changes in particle size distribution, morphology, crystallinity, and adsorption characteristics. According to XRD analysis, the degree of amorphization increased with grinding time, and the present crystalline phase in the final ball milled clay was found to be quartz, which was the associated phase in the original unmilled clay mineral. FTIR studies indicated the destruction of the layers of the montmorillonite upon milling. Adsorption experiments revealed that under similar conditions, BM-Clay2 has the most adsorption capacity for Ni(II) ions. Adsorption characteristics of this ball milled clay for the removal of Ni(II) ions from aqueous solutions was examined in batch adsorption studies under different conditions of contact time, solution pH, adsorbent dose, and initial Ni(II) concentration. The Langmuir maximum adsorption capacity was found to be 29.76 mg/g at pH 7 and 25 °C. The adsorption kinetics data showed better agreement with the pseudo second-order kinetic model. Also, both surface adsorption and intra-particle diffusion contributed to the rate limiting steps in the adsorption of Ni(II) on clay adsorbent. In conclusion, grinding of local clay using ball milling process can significantly increase the adsorption capacity of the clay for Ni(II) removal from aqueous solutions.



## 1. Introduction

Heavy metals in wastewater released from the waste discharge of industrial manufacturing processes are one of the major environmental concerns due to their toxicity, persistency, non-biodegradability, and accumulation in living organisms (Glatstein and Francisca, 2015; Jiang et al., 2010; Xing et al., 2011). In particular, nickel is released into aqueous systems from the manufacturing process of stainless steel, super alloys, metallic alloys, electroplating, batteries, etc. (Ijagbemi et al., 2009; Vieira et al., 2010a). Nickel exceeding its critical level, has been reported to be toxic and carcinogenic. It can cause health problems such as lung and kidney problems, gastrointestinal distress, headache and skin dermatitis (Dawodua and Akpomie, 2014; Fu and Wang, 2011; Ijagbemi et al., 2009; Vieira et al., 2010a). Different treatment techniques have been used to remove heavy metals from wastewater such as chemical precipitation, coagulation–flocculation, flotation, membrane filtration, electrochemical treatment technologies, ion exchange, and adsorption (Fu and Wang, 2011; Kurniawan et al., 2006). Among these methods, adsorption has been found to be one of the most effective, economical, and easy to adapt process for the removal of heavy metals from solutions (Qiu et al., 2015; Sis and Uysal, 2014).

Recently, clays or clay materials have gained much attention as the adsorbent. Clay minerals, which are important constituents of soil for immobilization of contaminants, play this role by taking up various pollutants as water flows over the soil or penetrates into the ground. Immobilization of contaminants takes place through either ion exchange or adsorption processes, or a combination of both. The high adsorption properties, non-toxicity, abundant availability, high specific surface area, mechanical stability, layered structure, and high cation exchange capacity (CEC), make clays and clay minerals to be attractive adsorbents for the removal of different pollutants (Djomgoue et al., 2012; Gupta and Bhattacharyya, 2008; Hao et al., 2014). A number of studies have been reported on the adsorption of Ni(II) by natural clays without any treatment including natural kaolinite and montmorillonite (Dawodua and Akpomie, 2014; Donat et al., 2005; Gupta and Bhattacharyya, 2008; Ijagbemi et al., 2009; Jiang et al., 2010; Shirvani et al., 2015;

* Corresponding author.
*E-mail addresses:* shmaleki@shirazu.ac.ir (S. Maleki), akarimi@shirazu.ac.ir, ajashni@yahoo.ca (A. Karimi-Jashni).

http://dx.doi.org/10.1016/j.clay.2016.12.008
0169-1317/

Vieira et al., 2010b). In addition, different modification techniques have been used for the improvement of clay quality and its characteristics, including intercalation and pillaring, and acid activation (Bhattacharyya and Gupta, 2008a). In recent years, various forms of modified clays have been used by researchers to remove Ni(II) ions from aqueous solutions (Bhattacharyya and Gupta, 2008b, 2008c; Ijagbemi et al., 2010).

It is well known that during dry grinding of mineral particles, mechanical effects cause surface, structural, and morphological changes (Djukić et al., 2013; Li et al., 2014). There are some reports on the effects of dry grinding on calcite (Li et al., 2014), palygorskite (Boudriche et al., 2014; Liu et al., 2012), and pyrophyllite (Zhang et al., 2015). In addition, grinding of clay minerals was the subject of several studies, namely the grinding of montmorillonite (Hrachová et al., 2007; Ramadan et al., 2010; Vdović et al., 2010) and kaolinite (Gamelas et al., 2014; Hamzaoui et al., 2015; Shahverdi-Shahraki et al., 2015; Valášková et al., 2011; Vdović et al., 2010; Zbik and Smart, 2005). These studies have focused on investigating the effects of dry grinding on the morphology, microstructure, aggregation, and changes of surface properties of particles, especially specific surface area and cation exchange capacity. Structural deformation caused by grinding such as distortion, fragmentation, and reduction of particle size, followed by an increase in specific surface area, exfoliation of particles and amorphization, can enhance the adsorption capacity of the clays (Dukić et al., 2015b).

Although numerous studies report the effect of mechanical grinding on the structure of clay minerals, only a limited number of them have investigated the role of particle size changes caused by ball milling of clay minerals on their ability for the removal of heavy metals from solutions (Djukić et al., 2013; Dukić et al., 2015a; Vhahangwele and Mugera, 2015).

This study aims to investigate the effects of ball milling process on the properties of the local clay minerals, including structural changes and adsorption capacity for the removal of Ni(II) ions from aqueous solutions. For that, the influence of different milling times and intensities on adsorption behavior of the clay was investigated. Moreover, the effects of contact time, solution pH, adsorbent dose, and initial metal solution concentration were investigated for the Ball Milled Clay (BM-Clay) with the highest adsorption capacity. Various adsorption isotherm and kinetic models were applied to describe the main mechanisms involved in the removal process.

## 2. Materials and methods

### 2.1. Preparation of clay sample

Natural local clay was obtained from Jahrom Mine, Fars province, south of Iran, and was purified by sedimentation technique as follows. The purified clay fraction was obtained by dispersing 10 g of clay lumps in 1 L distilled water, allowed to swell for 24 h, and stirred for 30 min. Then, the supernatant dispersion of particles was separated after about 2 min sedimentation and particles <2 μm were collected after 20 h. Finally, the collected clay was dried at 90 °C in oven and was ground to pass through a sieve with a pore size of 74 μm (200 mesh). Afterward, a dry grinding was performed as explained in the next section.

### 2.2. Ball milling of clay

Mechanical milling of clay minerals was carried out using a laboratory planetary ball mill consisting of two containers (7.0 cm inner diameter), using stainless balls with various diameters from 5 to 20 mm as milling media. In order to investigate the relationship between the grinding intensity and the rate of change of clay structure, various ratios of the weight of balls to powder including 10:1 and 20:1 were used. The milling speed was set at 500 rpm, and the grinding time varied from 5 to 20 h. Samples of Ball Milled Clay (BM-Clay) are denoted as Table 1 through the whole text.

**Table 1**
Characteristics of various BM-Clays.

| Clay name | Ball to powder weight ratio | Grinding time (h) |
|---|---|---|
| BM-Clay1 | 10:1 | 5 |
| BM-Clay2 | 10:1 | 10 |
| BM-Clay3 | 10:1 | 15 |
| BM-Clay4 | 10:1 | 20 |
| BM-Clay5 | 20:1 | 10 |
| BM-Clay6 | 20:1 | 20 |

### 2.3. Material characterization

The cation exchange capacity (CEC) of the purified clay was determined using the method described by Meier and Kahr (1999) by complex of copper ion with triethylenetetramine (Cu(II) sulfate: assay ≥99%, Merck, Germany; triethylenetetramine: assay ≥95%, Merck, Germany). The point of zero charge ($pH_{pzc}$) was determined using technique described by Lazarevića et al. (2007) and Ijagbemi et al. (2009).

The X-ray powder diffraction (XRD) patterns of the samples were measured using a Bruker D8 advance diffractometer with Cu-Kα radiation ($\lambda = 1.54$ Å) from 5° to 90° (2θ) in 0.05° steps. Chemical composition of the clay was determined by using X-ray fluorescence (XRF) spectroscopy (Philips PW1480).

The particle size distribution of samples were measured on dispersed particles in an appropriate dispersant using a dynamic light scattering particle size analyzer (Horiba LB-550), which covers ranges from 1 to 6000 nm. The method is based on the measurement of the laser light scattered from a sample cell that contains suspension. Ultrasonic disrupter UD-201 was used for dispersion of particles in the dispersant.

Morphologies and phase distribution in powder samples were analyzed by scanning electron microscope (SEM) TESCAN VEGA3 equipped with the energy dispersive X-ray spectroscopy (EDX) detector. The Fourier transform infrared spectra (FTIR) of the samples in the region 4000–400 $cm^{-1}$ were obtained in transmission by a PerkinElmer spectrum RX I using the KBr pellets technique.

### 2.4. Adsorption experiments

Standard solution of Ni(II) (1000 mg per liter) was prepared by dissolving certain amount of nickel sulfate ($NiSO_4 \cdot 6H_2O$) in distilled water, which was further diluted to the desired concentrations required for the adsorption experiments. Before the experiments, the initial pH of the Ni(II) solutions was adjusted using diluted HCl or NaOH. All chemicals used in this research were of analytical reagent grade (Merck, Germany).

Batch adsorption experiments were performed in 250 mL capped bottles by addition of various amounts of adsorbent into 100 mL of Nickel solutions and agitating in a temperature-controlled rotating shaker for a desired time interval. After the shaking procedure, the suspensions were centrifuged and concentrations of Ni(II) remaining in the supernatant liquid were measured with an air acetylene flame atomic adsorption spectrometer (Shimadzu A-A 680).

The removal of Ni(II) ions was studied as a function of pH (3.0–10.0), initial Ni(II) concentration (10–90 mg/L), contact time (0–1440 min), and clay amount (0.2–5.0 g/L). For the determination of adsorption isotherms, solutions of Ni(II) ions with different concentrations of 10 to 90 mg/L at pH 7 were agitated with 2 g/L of the adsorbent until equilibrium was achieved. The kinetics of adsorption was studied by investigating the Ni(II) ions uptake from the solution of 50 mg/L

Please cite this article as: Maleki, S., Karimi-Jashni, A., Effect of ball milling process on the structure of local clay and its adsorption performance for Ni(II) removal, Appl. Clay Sci. (2016), http://dx.doi.org/10.1016/j.clay.2016.12.008