Use of Nano-Porous Calcium Silicate for Heavy Metal Removal from Aqueous Solutions

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ABSTRACT

Water is indispensable for our life and fresh water resources are becoming rich by heavy metals particularly by industrial wastes. Heavy metals are very harmful to the living organisms and accumulated in the food chain. Removal of heavy metals are therefore very important for protection of ecological systems. In this study, nano-porous calcium silicate produced from Rice Hull Ash in the laboratory, was used for the adsorption of copper, lead and zinc ions from an aqueous solution. The three elements – copper, lead and zinc – were adsorbed on the calcium silicate surface in ratios of 90-96 % in the first 15 minutes. Before and after the adsorption experiments, FTIR analyses of calcium silicate samples were done to investigate the adsorption type which can be chemical or physical.

**Keywords:** Nano-porous, calcium silicate, heavy metal, adsorption, FTIR spectra

INTRODUCTION

Industrial wastes containing heavy metals, especially lead, zinc and copper are polluting the environments and our potable water sources in a dangerous way. The removal of these metals from aqueous solutions and wastes is therefore much more important than ever today. Adsorption is the most popular process for removing the heavy metals from waters today. Activated carbon is very effectively used in the adsorption of heavy metals and several materials from aqueous solutions; but it is still expensive and necessitates the development and use of new materials (Anupam et al., 2011, Souza et al., 2018, Dai et al., 2017).

Calcium silicate is present in nature (Teir et al., 2005) as wollasonite mineral. Nano-structured calcium silicate however, is synthetically produced with several functional groups and has the characteristics for different applications in the industry today (Bormann et al., 2004; Johnston et al, 2008, 2011; Sadic et al., 2010; Taspinar et al., 2013). Calcium silicate is especially used to remove Endotoxin which is present in the outer cell membranes of gram negative E-coli bacteria, (Wang et al., 2005). Because of cake permeability character, it's also used for the preparation of oral solid Gentamicin (GM) which is very effective anti-bacterial agent against the gram positive cocci and gram negative bacilli infections (Ito et al., 2005).

Johnston et al. (2008) have made broad studies on nano-structured calcium silicate. They showed that it is used in many areas such as preparation of calcium silicate-carbon nano tubes; heat storage and controlled release of heat, liquids and gases; catalyst support in the photo catalytic reactions due to its high surface area; selectively removal of metal ions, oils, phenols,

phosphates and several pollutants from liquids, aqueous solutions and gases; in the anti-bacterial and anti-corrosion applications especially in the pharmaceuticals and functional packaging industries, etc. Because of its strength and whiteness, it is also used in ceramic, paper and plastic industries very widely.
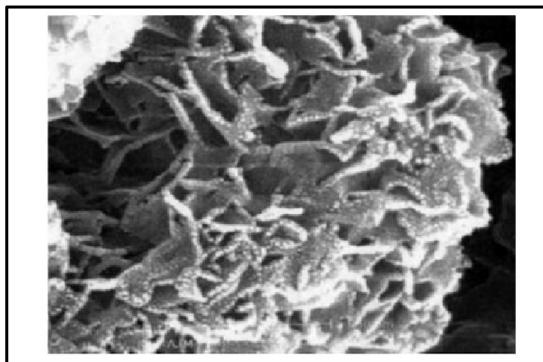
Figure 1. Open frame nano-structured calcium silicate sample SEM image (Johnston et al., 2008)

MATERIAL AND METHODS

Materials

Reagents used for the production of nano-structured calcium silicate were sodium silicate produced in the laboratory (production process is outlined in the "Methods" section), reagent grade anhydrous calcium chloride and distilled water. Aqueous solutions of lead, zinc and copper ions were prepared using reagent grade $Pb(CH_3COOH)_2 \cdot 3H_2O$, $ZnSO_4 \cdot 7H_2O$, $Cu(CH_3COOH)_2 \cdot H_2O$, respectively.

Methods

Nano-structured calcium silicate used in the removal of heavy metal ions in the experiments was produced from the Rice Hull Ash (RHA) which is an agricultural waste from a Rice Mill in Thrace region in Turkey. The original RHA from the factory was burned once again to remove all carbonaceous materials. Then, the Re-burned RHA was boiled for with NaOH to extract the siliceous materials in the form of sodium silicate. Sodium silicate solution then was treated with the calculated amount of $CaCl_2$ solution and calcium silicate was obtained by the precipitation reaction given in the Eq. (1).

$$Na_2SiO_3(aq) \ + \ CaCl_2(aq) \ \rightarrow \ CaO.nSiO_2.mH_2O \ + \ 2NaCl \qquad (1)$$

For the adsorption studies an orbital shaker was used. The experiments were conducted at room temperature ($20\text{-}25^0C$) at different pH's, different adsorption times and different amounts of adsorbent (calcium silicate).

The chemical analysis of Pb, Zn and Cu ions in the aqueous solution was done Atomic

Adsorption Spectrophotometer (AAS). For the surface area and particle size measurements BET (Brunaur-Emmett-Teller) and Micrometrics ASAP 2000 Interface Controller were used, respectively. For determining the changes on the surfaces after heavy metal adsorption of the calcium silicate, the FTIR-ATR was used.

RESULTS AND DISCUSSION

The calcium silicate sample produced at above conditions in our previous studies (Pourshakiba, 2012) was analyzed and its chemical composition was found as 49% SiO_2, 14% CaO w/w. The amount of crystal water was around 18-20% and the impurities coming from the alkaline extraction of the Re-burned RHA. The average particle size of the calcium silicate sample was measured as 4.5μ. Surface area measurements with BET apparatus applying degassing at 130^0C for 18-20 h has given a 141 m^2/g value of the calcium silicate product. TEM picture of nano-structured calcium silicate produced in our laboratory and used in the experiments is given in Fig.2.
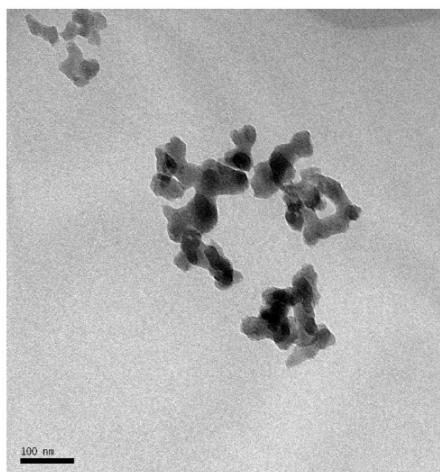
Figure 2. TEM image of water washed calcium silicate sample produced in our previous work and used in present experiments (Pourshakiba, 2012).

Adsorption Studies

0.1 g of calcium silicate samples were treated with lead, zinc and copper solutions separately at room temperature at pH 5 for 2 h on the orbital shaker. Then the mixture was filtered and the chemical analysis of the ions in the supernatant and the FTIR analysis of the dried calcium silicate samples were done. The adsorption capacities of calcium silicate for each lead, zinc and copper ions then calculated. The results are given in Table 1 and in the Fig. 3.

Table 1. The change of the Pb^{+2}, Zn^{+2} and Cu^{+2} ion adsorption capacities of calcium silicate samples with time (at the pre-determined initial concentrations of Pb^{+2} : 100 ppm, Cu^{+2} : 12ppm, Zn^{+2} : 3 ppm) at pH 5 and 0.1 g adsorbent amount.

	Time (min)			
	15	60	120	240
Pb^{+2} adsorption %, w/w	89.79	96.25	96.73	99.30
Zn^{+2} adsorption %, w/w	91.80	49.76	54.83	73.93
Cu^{+2} adsorption %, w/w	95.83	98.33	98.50	98.75

As it is seen from Table 1, about the 90-96 % of the three metal ions were adsorbed in 15 min. on the calcium silicate samples. Pb^{+2} and Cu^{+2} ions adsorption increased in time and reached almost to completion (99 %) in 4 h. However, Zn^{+2} ion adsorption did not show the same tendency. After first quick adsorption, it is started to be desorbed from the surface in 2 h; then started once again to be adsorbed gradually around 4h. The adsorption mechanism of Zn^{+2} ions seems different from those of Pb^{+2} and Cu^{+2} ions.

The results of FTIR-ATR studies are shown in Fig. 3. As it is clear in this Fig.3, there is not any new peak in the spectrum of calcium silicate sample before and after the copper adsorption but the peak strengths are weakened and the peaks are shifted. The strength of the peak at 1006cm^{-1} belonging to SiO_2 is lowered and shifted to 1071cm^{-1} after copper adsorption. The peak belonging to crystal water at 1459cm^{-1} was also weakened and shifted to 1459cm^{-1} after adsorption of copper. It can be said from these data that, the adsorption of copper on the calcium silicate is not chemical, but it is trapped in its nano-pores. The reason of this shifting and weakening of the peaks after copper adsorption is also explained by several workers in literature (Li et al., 2010, Saravanapavan and Hench, 2003); as due to the weakening of the SiO_2-Ca bond in the $CaSiO_3.xH_2O$ structure, after Cu^{+2} ions adsorption at the surface. And that kind of adsorption of the metal ions on calcium silicate surfaces were defined as "*chemical adsorption*" besides "*physical adsorption*".

Similar results were also found in our previous studies done in the same laboratories (Oglakci and Baglar, 2010, Taspinar et al. 2011). According to these studies, the three metals are adsorbed at pH 5 almost to completion and desorbed at pH 3 from the calcium silicate surface.
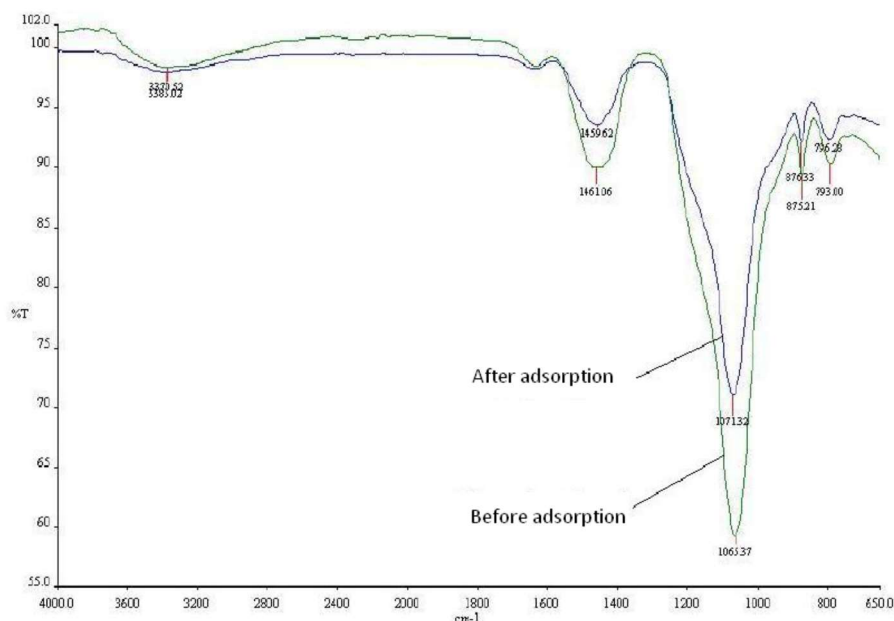
Figure 3. FTIR_ATR spectrum of calcium silicate sample before and after Cu^{+2} ions adsorption.

CONCLUSION

Calcium silicate seems as a good adsorbent for heavy metal ions, lead, copper and zinc from aqueous solutions around pH 5. Although the three elements are adsorbed very fast in 15 min; the complete adsorption over than 99 % necessitates at least 2 h. Zinc adsorption however is different from copper and lead; and it is desorbed from the surface as the time longer than 15 min. FTIR-ATR studies also support the adsorption mechanism of especially copper ions; which are probably adsorbed also chemically, besides physical adsorption at the same time.

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