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Non-acidic synthesis of phosphatized dolomite and its sorption behaviour towards Pb $^{2+}$, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+} and Co^{2+} ions in multicomponent aqueous solution

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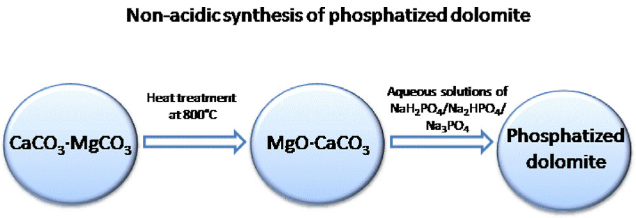
HIGHLIGHTS

- The soft non-acidic method for preparing high performance granular phosphate sorbents was proposed.
- Up to 90%–95% of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+} and Co^{2+} was removed from multicomponent aqueous solutions in dynamic mode.
- Cost-effective metal ions removal was achieved using phosphatized dolomite.
- The influence of phase, chemical composition and surface properties of sorbents on their behaviour towards bivalent metal ions was discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work proposes the soft non-acidic method for preparing granular phosphate sorbents under standard conditions (25 °C, 101.3 kPa) using thermally activated dolomite as a cheap source of Ca and Mg, with NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 aqueous solutions as phosphating reagents. The effect of the reagents' properties and contact time on the phase and chemical compositions, adsorption and textural properties of the obtained sorbents was studied. The most effective sorbents were highly efficient. Up to 90%–95% of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+} and Co^{2+} was removed from multicomponent aqueous solutions in dynamic mode (at initial concentrations of 5 mg L^{-1}, linear velocity 10 m h^{-1}). The influence of phase, chemical composition and surface properties of sorbents on their behaviour towards bivalent metal ions was also discussed.

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1. Introduction

Contamination of water and soil by heavy metal ions is a serious problem which impacts significantly on agriculture, drinking water quality and ecosystems (Bradl, 2005). The permissible concentration of heavy metal ions in wastewater and drinking water ranges from a few ppm to ppb (WHO, 2011). Wastewater treatment methods include precipitation, coagulation, reverse osmosis, ion exchange (Naushad and ALOthman, 2015; Bushraa et al., 2015) and sorption (Alqadami et al., 2016; Naushad et al., 2016). Due to its high effectiveness, economy and simplicity of operation, sorption widely used for environmental processes (Fu and Wang, 2011). Importantly, sorption is the only method to selectively remove heavy metal ions from salt-containing aqueous media without changing their basic mineralogical composition, which is useful for treating sea water polluted with heavy metal ions or purifying natural mineral water for drinking purposes (Hashim et al., 2011; Naushad et al., 2015).

Phosphate is widely used to remove metal ions from water and soil and was first proposed by Nriagu in his research on lead orthophosphate (Nriagu, 1974). Intensive investigation into the use of phosphates for water purification and remediation of contaminated soils followed, as evidenced by the large number of scientific publications (Cao and Ma, 2003; Xenidis et al., 2010; Thawornchaisit and Polprasert, 2009; Hashimoto et al., 2009). The removal of heavy metal ions with phosphates is based on the formation of insoluble forms of the extracted metals. Two principally different sources of phosphates are used: 1—soluble (phosphoric acid, potassium and sodium phosphates) and 2—low-solubility phosphate compounds (natural and synthetic materials based on hydroxyapatite [HA] and calcium, titanium and zirconium phosphates). The main drawback of soluble forms is the need to constantly and accurately control the phosphate dose, as a high concentration of phosphate ions pollutes both water and soil. Therefore, low-solubility forms of phosphate are more promising and safe to use (Mignard et al., 2012; Park and Bolan, 2011).

HA is the most studied phosphate compound sorbent of heavy metal ions (Choudhury et al., 2015; Khal and Batis, 2015; Corami et al., 2008). Yet calcium and magnesium phosphates, with their non-apatite structure, have a higher sorption capacity than HA (Ding et al., 2015; Sugiyama et al., 2003). Therefore common and cheap natural minerals such as calcite and dolomite are promising sources of Ca and Mg for phosphate sorbents from technical and economical point of view. The acid method is most widely used; dissolving natural raw materials in mineral acids with subsequent precipitation by ammonium phosphates or neutralization of carbonates by phosphoric acid (Ivanets et al., 2016). Non-acidic soft methods are a better alternative, as they do not require corrosive chemicals and are more environmentally friendly.

To the best of our knowledge, there is a limited amount of existing research on non-acidic synthesis of calcium phosphates from calcium carbonate and an aqueous solution of potassium dihydrogen phosphate (Sebei et al., 2015; Minh et al., 2012). The main product of the interaction was HA, which had higher sorption properties than HA sorbents described elsewhere. Sebei, Minh et al. explain the formation of HA with low crystallinity by the presence of reaction by-products (tricalcium phosphate, hydrophosphate and calcium dihydrogen phosphate) and impurities of unreacted calcium carbonate. It is important to note that powdered sorbents are mostly investigated, but water treatment is more efficient in dynamic mode, which requires the use of granular sorbents.

Preliminary studies have produced highly effective phosphate absorbents using thermally activated dolomite in aqueous sodium phosphate solutions. The powdered products of phosphatized dolomite obtained by a non-acidic method demonstrated a high sorption capacity (from 1.5 to 6.8 mmol g^{-1}) for Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+} and Co^{2+} ions (Ivanets et al., 2015).

The novelty of this study is to solve the environmental problem by using a green preparation method. Specifically, a soft non-acidic method of obtaining highly effective granular sorbents based on phosphatized dolomite is proposed here. Importantly, the suggested method allow to obtain sorbents using thermally activated granular dolomite as a cheap source of Ca and Mg and NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 aqueous solutions as phosphating reagents. The products of a dolomite interaction with sodium phosphates were investigated for their behaviour as sorbents of Pb^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, Sr^{2+} and Co^{2+} ions, taking into account the composition and surface characterization of the sorbents.

2. Experimental

2.1. Preparation of phosphate sorbents

Natural dolomite deposits from Ruba (Belarus) with the chemical composition (wt. %) CaO—30.3, MgO—20.0, SiO_2—1.1, Fe_2O_3—0.4, Al_2O_3—0.5, SO_3—0.4, K_2O—0.2, Na_2O—0.1 were used as the starting material for sorbent preparation. A 1.6–2.5 mm fraction of dolomite was calcined in an electric oven at 800 °C for 5 h (temperature increase rate 5° min^{-1}). Aqueous solutions with 0.2 M concentration were prepared by dissolution of $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot 12H_2O$. All chemicals were of analytical grade and utilized as purchased from Sigma-Aldrich without further purification. The ratio of phosphating solution volume to dolomite weight was 33 : 1.4 ml g^{-1}. Theoretical calculations suggest that this quantity is enough for full interaction between magnesium oxide and sodium phosphates.