Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 2649–2658

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Removal and slow release studies of phosphate on surfactant loaded hydrothermally synthesized silicate nanoparticles

Deepesh Bhardwaj [a,*], Pankaj Sharma [b,*], Monika Sharma [c], Radha Tomar [d]

[a] *Institute of Information Technology and Management, Gwalior 474001, India*
[b] *Graduate School of Green Energy Technology, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 305-764, Republic of Korea*
[c] *Clean Fuel Department, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea*
[d] *School of Studies in Chemistry, Jiwaji University, Gwalior, India*

ARTICLE INFO

Article history:
Received 11 April 2014
Received in revised form 14 July 2014
Accepted 14 July 2014
Available online 8 August 2014

Keywords:
Phosphate
Adsorption
Nanoparticles
Surfactant modification
Slow release fertilizer

ABSTRACT

The reported work is mainly focused on the use of as-synthesized silicates (clinoptilolite and montmorillonite) nanoparticles and their surfactant modified forms for the removal and slow release formulation of phosphate. Batch experiments have been carried out to determine the influence of parameters like initial phosphate concentration, pH of the medium, contact time between the adsorbate and adsorbent, weight of adsorbent, and system temperature on phosphate removal. Furthermore, slow phosphate release studies have been performed by thin layer-funnel analytical test and soil column percolating system. The results of batch adsorption studies reveal that surfactant modified forms of clinoptilolite and montmorillonite show better adsorption potential for phosphate than their unmodified form and phosphate removal ability of surfactant modified silicates increases with increasing amount of loaded surfactant. The maximum adsorption of phosphate is observed around pH 7 and maximum Langmuir monolayer phosphate adsorption capacity 93.46 mg g^{-1} is observed for hexadecyltrimethylammonium ($CH_3(CH_2)_{15}N^+(CH_3)_3$) loaded clinoptilolite (HC). The obtained results indicate that surfactant loaded silicates are very good adsorbent for phosphate removal and slow release of phosphate is also achievable as it releases phosphate still after 15 days of leaching.

1. Introduction

As phosphorus is one of the important elements for agricultural and industrial development therefore, large quantities of phosphates are often observed in domestic wastewater, groundwater and industrial wastewaters. Phosphorus removal from wastewater before its discharge into receiving waterways is of considerable significance to protect natural water streams from eutrophication [1–3]. The eutrophication disposition of water bodies that are receptacles of chronic and episodic delivery of phosphate and the concomitant negative environmental impact has been chronicled [1]. To control eutrophication, the recommended concentration of total P should not exceed 0.005–0.1 mg L^{-1} in natural water bodies [4].

Several physical, biological and chemical processes have been reported in the literature for phosphates removal from aqueous system. These processes include adsorption, ion exchange, precipitation, membrane filtration, reverse osmosis, etc. Out of these methods adsorption process is considered as promising water treatment technique because it is simple and economical and results in less sludge production due to which it cause minimal disposal problems. Further, this process is also able to handle shock loadings and operable over a wide range of temperatures. In recent years, application of efficient solid adsorbent/ion-exchanger involving natural and synthesized materials for phosphate removal from aqueous solutions has been widely investigated [5–7]. Silicates (zeolites and clays) are one of such materials having high phosphate adsorption capacity [8–11]. In spite of having high adsorption capacity, ion-exchange characteristic, porous nature, cage like structure and high surface area, applicative aspect of silicates for phosphate removal is barely reported. The reason for non-applicability of zeolites for anions removal from aqueous waste is its negatively charged structural framework due to isomorphic substitution of aluminum for silicon. Thus, loading of anions like phosphate (PO_4^{3-}) onto its surface will be negligible due to coulombic forces of repulsion [12]. Therefore, an alteration in surface charge property by using appropriate charge reversal

---

* Corresponding author. Tel.: +91 9977672671.
E-mail addresses: bhardwajdeepesh@gmail.com (D. Bhardwaj), sharmapankaj47@yahoo.com (P. Sharma).

http://dx.doi.org/10.1016/j.jtice.2014.07.010
1876-1070/

chemical species makes silicates such as zeolite (clinoptilolite) and clay (montmorillonite) suitable for phosphate removal from aqueous system [13,14]. In literature, only selected number of papers exists regarding the use of surfactant modified silicates for the removal of anionic species mainly nitrate from the contaminated waste water [14–16]. In general, surfactant loading enhances the adsorption capacities of the adsorbents. So, our studies aimed to probe the adsorption potential of surfactant modified as-synthesized nano-sized silicates for the removal of phosphate from aqueous waste. In this work we have used hydrothermally synthesized clinoptilolite and montmorillonite nano-particles (Fig. 1) with and without surface modification. The surface charge reversal of clinoptilolite and montmorillonite has been made by treating these with two cationic surfactants hexadecyltrimethylammonium (HDTMA) and dioctadecyldimethylammonium ($(CH_3(CH_2)_{17})_2N^+(CH_3)_2$, DODMA) separately. In this paper HDTMA and DODMA loaded clinoptilolite are abbreviated as HC and DC respectively whereas HDTMA and DODMA loaded montmorillonite as HM and DM. The present work also aims to demonstrate the performance of phosphate loaded surfactant modified silicates as slow release phosphate materials. The phosphate percentage removal and effect of various process variables (pH, adsorbent dose, equilibration time, amount of loaded surfactant, organic matter, temperature and initial phosphate concentration) on adsorption process are used as performance indicators. The adsorption isotherm models were used to fit the experimental data to estimate adsorption capacity and rate parameters which can aid in system design.

2. Materials and methods

2.1. Materials

Two laboratory synthesized materials which belong to two different silicate families (tectosilicates and phyllosilicates) have been used as adsorbent for this study. The detailed process of clinoptilolite and montmorillonite synthesis is described in our previous publication [14]. The surfactants selected for this study *i.e.*, hexadecyltrimethylammonium bromide ($CH_3(CH_2)_{15}N(Br)(CH_3)_3$) and dioctadecyldimethylammonium bromide ($(CH_3(CH_2)_{17})_2N(Br)(CH_3)_2$) were obtained from Sigma-Aldrich whereas monopotassium phosphate (KH_2PO_4) was supplied by E Merck (India) Limited. All these chemicals were used as such without any further purification.

2.2. Surface modification of clinoptilolite and montmorillonite

A known quantity (200 mg) of washed silicate samples is mixed with 100 mL surfactant solutions (250, 500, 750 and 1000 mg L^{-1}) prepared in 1:1 ratio (v/v) ethanol:deionized water (DIW) solution. The water–alcohol solution has been used in order to improve the solubility of surfactants. The resulting suspensions are shaken at room temperature for 24 h, and then centrifuged, washed with ethanol–DIW solution until no Br^- has been detected by $AgNO_3$ test. The residual surfactant concentration in the supernatant was determined spectrophotometrically and the loaded amount of surfactant has been estimated from the difference of surfactant concentration in the aqueous phase before and after loading. These modified zeolites were ground in an agate mortar, freeze dried and stored in vacuum desiccators for further use [14,17]. Furthermore, characterization, adsorption studies and slow release formulation experiments have been made with the materials obtained after loading with 1000 mg L^{-1} solution of surfactants only.

2.3. Batch adsorption studies

The phosphate adsorption experiments were conducted using aqueous solution prepared by dissolution of an appropriate amount of monopotassium phosphate in DIW (340 mg L^{-1}). Batch experiment mode was adopted due to its reliability and simplicity. Batch adsorption studies have been carried out in stopper conical flasks containing 50 mL of monopotassium phosphate solution of concentration 340 mg L^{-1} and 200 mg of adsorbent. The initial pH of solution was adjusted using dilute solutions of HCl and NaOH to a definite value before the start of experiment. The reaction mixture was then placed in thermostatic water-bath shaker at fixed temperature for desired time followed by filtration.

The left out concentration in the supernatant solution after adsorption process was analyzed spectrophotometrically on Systronics 114 UV–visible spectrophotometer by measuring absorbance at λ_{max} of 420 nm. As we know that phosphate reacts with ammonium molybdate in acidic conditions to form molybdophosphoric acid which gives blue color on $SnCl_2$ addition and shows absorbance maxima at 420 nm. So, amount of phosphate adsorbed on the surface of adsorbent can easily be determined. To optimize the adsorption process the influence of specific process parameters such as pH, adsorbent dose, equilibration time, amount of loaded surfactant, organic matter, temperature, and initial phosphate concentration on phosphate adsorption has been investigated by changing one parameter and keeping other parameters constant. All the experiments were carried out in

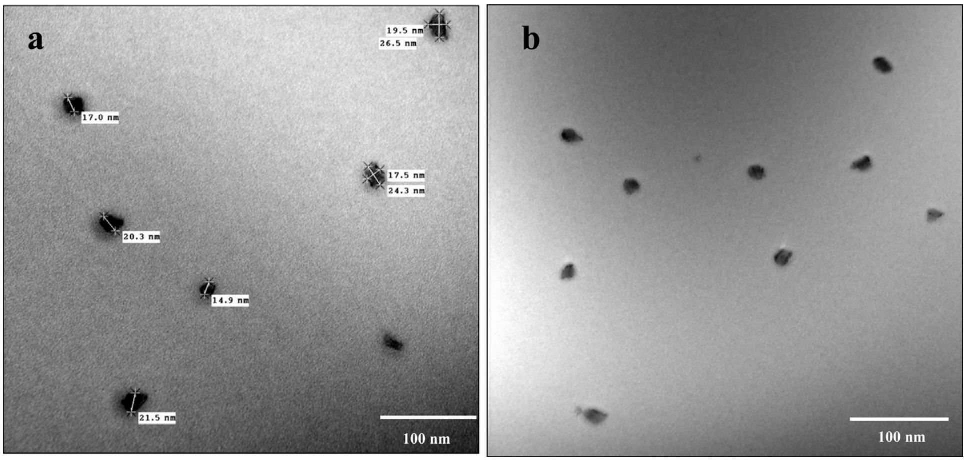

Fig. 1. Transmission electron microscopic images of clinoptilolite and montmorillonite. Reproduced with permission of Elsevier [14].