



Utilization of nano-alumina and activated charcoal for phosphate removal from wastewater



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ABSTRACT

Nano-alumina (NA) and activated charcoal (AC) were compared as adsorbents to remove phosphate from aqueous wastewater. Batch-mode adsorption experiments were carried out to investigate the use of two commercially available adsorbents for the removal of phosphate from synthetic wastewater/solution. Effect of time, adsorbent dosage, pH and temperature was evaluated. Results revealed that maximum phosphate removal of 90.2% was achieved in 120 min at pH 6 using 3.2 g/L of dosage with activated charcoal whereas 100% removal was observed at pH 6 with nano-alumina at 90 min using 1.6 g/L of adsorbent dose. The equilibrium data was applied to Langmuir, Freundlich, Tempkin, Dubinin-rudkavich isotherm models. Results revealed that Langmuir isotherm model and pseudo-second order kinetic model were found best fitted for both the adsorbents, having good correlation R^2 value (0.999 and 0.938). The value of enthalpy (ΔH) calculated from the thermodynamic parameters revealed that adsorption process is endothermic for both adsorbents. Characterization of both adsorbents done with XRD shows their amorphous and crystalline nature while FTIR of the adsorbents shows the interaction of adsorbent and adsorbate of solution. Morphology of both adsorbent shows the porous nature of adsorbents which indicates their efficiency in wastewater treatment. Study clearly indicates that the removal potential of nano-alumina is more as compared to the activated charcoal.

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1. Introduction

Water pollution is one of the major global concern as rise in population, urbanization and industrialization are further intensifying the issue (Huang et al., 2015). Discharge of effluents from the industries and domestic wastewater including runoff from agricultural land are some of the major sources of freshwater pollution (Zong et al., 2013). In developing countries 70–80% of all ill health is due to water contamination wherein women and children are more susceptible to water pollutants. The potability of natural waters sources has been highly reduced due to the discharge of toxic pollutants in water bodies (Afkhani et al., 2007; Bhatnagar and Sillanpää, 2011; Kumar et al., 2011). The agricultural fields and domestic waste are one of the major contributors for contaminating water that releases high concentration of phosphate. Further, a number of surface water bodies like lakes, coastal areas, etc. are highly

affected due to increase in nutrients (phosphate) and other pollutants leading to problems of rapid growth of algae and hyacinth, thereby, causing eutrophication like conditions (Fulazzaky et al., 2014). The harmful effects of eutrophication includes depletion of oxygen, killing of fish, murky water and depletion of flora and fauna (Rout et al., 2014). Kilpimaa et al. (2015) highlighted that eutrophication occur even when trace amount of phosphate concentration is (0.02 mg/l) in the surface water.

Increasing phosphate concentration due to water pollution demands more attention towards its treatment (Zhang et al., 2011). Since adsorption is consider as one of the cost effective method of wastewater treatment, however as highlighted by Mor et al. (2016) there is a need to explore adsorbents which have rapid adsorption properties for the treatment of wastewater. Adsorbents having fast adsorption rate and high adsorption capacity are extremely demanded for wastewater treatment. Various natural adsorbents like peat, sawdust, clay minerals, agricultural residue, ores and iron oxide are being widely used for removing wide range of contaminants including cations, anions and heavy metals (Huang et al., 2014; Maiti et al., 2012; Ugurlu, 1998). Therefore, activated charcoal and nano alumina have been proved to be the most popular

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Table 1
Properties of nano-alumina and activated charcoal.

Properties	Activated charcoal	Nano-alumina
Surface area	1000 m ² /g (BET)	>40m ² /g (BET)
Melting point	3652 °C	2040 °C (lit)
Description	Carbon	Alumina
Form	Black powder	Nanopowder
Particle Size	70–100 mesh	<50 nm (TEM)

and most reliable adsorbents for the wastewater treatment. Activated charcoal has been used traditionally for the removal of trace pollutants such as odor, color and taste (Tang et al., 2012). Microporous characters, high surface area and their chemical nature have proved that activated carbons have potential for the extraction of pollutants from wastewater. In addition, separation risen as mentioned by Qadeer (2013) high adsorption capacity and adaptability of activated carbon broadens its application. According to literature, phosphate removal efficiency of 94.9% was achieved at the dosage of 147.5 mg/l over red mud poly aluminum chloride (Fan et al., 2015), Kim et al. (2016) reported 95% removal by using iron oxide nanotube at 30 min of time from synthetic wastewater, maximum 88.3% phosphate removal was observed using iron-nanoparticle nanoparticle (Arshadi et al., 2014), removal up to 95% was achieved at 1 min of time using iron hydroxide nano-particle (Zelmanov and Semiat, 2015), adsorption of 0.28 mmol/g was noticed on Mg-Al layered double hydroxide (Halajnia et al., 2013), 68.3% removal was achieved at 30 min of time by graphene zero-valent iron (Liu et al., 2014), magnetic diatomite clay adsorbed 78.7% phosphate removal at 30 min of time (Chen et al., 2016). However, there are limited studies, which studied the removal of phosphate from wastewater using activated charcoal. Activated charcoal, developed from many other raw materials has been used for the treatment of ions such as lead, copper, color, cobalt, mercury etc. Singh et al. (2008) reported 97.9% lead (Pb) removal at 3 g/l dosage and 6.5 pH using activated carbon prepared from tamarind wood, fluoride removal up to 40.2% was achieved at 5 mg/l and 6.0 pH using carbon sugarcane bagasse (Yadav et al., 2013), removal of 80% was reported at 100 mg/l by granular activated carbon for orthophosphate removal (Hussain et al., 2011), colour reduction of 98% was achieved using powdered activated charcoal at pH 3 (Bernal et al., 2016). The current study highlights efficiency of two commercially available adsorbents i.e. nano-alumina and activated charcoal for the removal of phosphate ions from the synthetic wastewater.

2. Material and methods

2.1. Adsorbents and adsorbate solution

Nano alumina (NA) and Activated Charcoal (AC) material for the experiment were obtained from market. The nano-oxide used in this work was alumina powder (Al₂O₃) having particle size <50 nm of Sigma Aldrich and activated charcoal (AC) from Fisher Scientific Ltd. was used as such for the experiment. The properties of adsorbents used for the removal of phosphate are listed in Table 1. The adsorbate solution was prepared by dissolving anhydrous potassium dihydrogen phosphate (KH₂PO₄) in double distilled water. This stock solution of known concentration was used for serial dilution to get the required concentration

2.2. Batch experiment

Batch mode setup was employed by varying different parameters such as pH, time, amount of adsorbent and temperature at shaking the flask at a constant speed. Phosphate solutions were prepared from stock solution by dilution of 1000 ppm to 10 ppm

of phosphate solution. Removal efficiency of phosphate was measured using following equation:

$$\% \text{Removal of phosphate} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

In the above equation C₀ represent initial concentration whereas C_e as final level of phosphate (mg/L) in aqueous solution.

2.3. Characterization of adsorbents

Adsorbents were characterized using the approach as detailed earlier by Mor et al. (2016).

2.4. Adsorption isotherms and kinetic studies

Isotherm models are important to understand the sorption mechanism, which indicates interaction between the adsorbate concentration and quantity of phosphate adsorbed by nano-alumina & activated charcoal. Results attained from the batch mode set up were studied by using different isotherm models and kinetic model.

Langmuir isotherm, the sorption takes place at specific homogeneous sites on the surface of the adsorbents. It is assumed that once a sorbate molecule occupies sites, no further sorption takes place at that site (Subbaiah and Kim, 2016). The Langmuir isotherm equation as mentioned below:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} b + \frac{C_e}{q_{\max}} \quad (2)$$

The q_{max} represents maximum adsorption capacity while b is the Langmuir constant representing adsorption energy. The plots between C_e/q_e and C_e was used to derive Langmuir parameters.

This isotherm predicts the heterogeneous surface adsorption sites of adsorbents. Thus, infinite surface coverage by indicating the multilayer sorption of the surface. Eq. (3) represents Freundlich adsorption isotherm equation is represented below:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

K_f Freundlich constants and n adsorption intensity. It can be calculated from the linear plots of log q_e vs. log C_e.

Templekin isotherm model describe the chemical adsorption process as electrostatic interaction (Fan et al., 2016). The Templekin model equation is explained below:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (4)$$

Where K_T is equilibrium binding constant and B₁ is the heat of the adsorption. The value of K_T and B₁ are attained by using linear plot q_e against the ln C_e.

The Dubinin-Redushkevich (D-R) isotherm was applied to understand the nature of adsorption process and the Dubinin-Redushkevich isotherm as under:

$$\ln q_e = K^2_e + \ln q_{DR} \quad (5)$$

Polani potential (ε) is given as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

Where q_s is the maximum capacity adsorbent to adsorbed the adsorbate, B energy constant, R is gas constant and t is temperature. Adsorption mean free energy can be derived from D-R constants using following equation:

$$E = \frac{1}{(2B)^{1/2}} \quad (7)$$

The chemical and physical characteristics of the adsorption mechanism is calculated by adsorption energy (E).

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