Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue

*Deepak Yadav, Meghna Kapur, Pradeep Kumar, Monoj Kumar Mondal**

Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, India

ABSTRACT

The aim of the present study was to investigate the possible use of fruit juice (*Citrus limetta*) residue and rice husk as adsorbents for phosphate removal from aqueous solutions. Batch experiments were performed to achieve maximal phosphate removal by varying process parameters, like pH, contact time, temperature, adsorbent dose and initial solute concentration. FTIR studies revealed that O—H, N—O and C—N groups are responsible for phosphate binding process. The maximum removal of phosphate was achieved as 95.85% at 298 K, adsorbent dose 3 g/L and pH 6.0 with acid treated fruit juice residue. Adsorption process was fitted with pseudo-first order kinetics at 298, 308 and 318 K, respectively. Various isotherm models and mass transfer mechanisms were studied for the removal of phosphate ions from aqueous solutions. Among various adsorption isotherms, Freundlich isotherm showed a better correlation with experimental data. The adsorption energy calculated from Dubinin–Radushkevich isotherm for the most efficient adsorbent indicated physical nature of adsorption.

Keywords: Adsorption; Activated fruit juice residue; Phosphate; Activated rice husk; Batch process

1. Introduction

Phosphate enjoys the company of rest two macronutrients nitrogen and potassium and contributes in plant growth, human body upbringing and aquatic life survival. Phosphate is an inorganic element mined from hard phosphate rocks produced in America, China, Morocco, etc. and used as an irreplaceable plant growth nutrient because it allows the transfer of energy within plants cells, required in adequate level to stimulate growth and create changes to plant maturity. Phosphate is present as an ingredient in NPK (nitrogen, phosphorus, and potassium) fertilizer.

The reserves of phosphate in soil are basically in the form of mineral phosphate and organic phosphate. Mineral phosphate, as the name suggests is the insoluble and strongly absorbed phosphate that exists in most soils. It is not available to plants as such through chemical transformation within the soil small amounts do become soluble and available. The organic phosphate is the return of organic crop residues, compost and farm yard manures. It is dependent on the microbial activity in the soil. This living activity mineralizes the phosphates from the residues and makes them available to the plant (as one of the limiting macronutrients). The overabundance of phosphate in water (i.e. >0.1 mg/L) (USEPA, 1996) stimulate algal growth and other vegetation that consumes so much dissolved oxygen that an insufficient amount remains for aquatic life, cause eutrophication which is a danger for the denizen of water and the whole ecosystem in broader prospective. This nutrient loading affects water quality, aquatic life, cascading effect as well as increase the cost of water treatment. The permissible level of phosphorus in the water to prevent algae growth is 0.05 mg/L (Benyoucef and Amrani, 2011). Physical, chemical and biological treatment methods have been developed to remove aqueous phosphate prior to their discharge into natural water bodies and runoff (Bashan and Bashan, 2004; Morse et al., 1998; de Haas et al., 2000). Typically, phosphate is removed by adding aluminum, iron or calcium-based chemicals to separate it from the wastewater and

---

* Corresponding author. Tel.: +91 9452196638; fax: +91 5422367098.
E-mail address: mkmondal13@yahoo.com (M.K. Mondal).

Received 19 May 2014; Received in revised form 8 August 2014; Accepted 25 September 2014
http://dx.doi.org/10.1016/j.psep.2014.09.005
0957-5820/© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Please cite this article in press as: Yadav, D., et al., Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue. Process Safety and Environmental Protection (2014), http://dx.doi.org/10.1016/j.psep.2014.09.005

allowing it to settle out (Zeng et al., 2004). Other processes force bacteria to consume and remove phosphate, which can be done by varying the amount of oxygen available to the bacteria. This is known as biological phosphorus removal (Sedlak, 1991). Other few techniques of phosphate removal are chemical precipitation (Oguz et al., 2003), advanced oxidation process (Crittenden et al., 2005), ion exchange (Kuzawa et al., 2006), enhanced biological phosphorus removal (Rittman and McCarty, 2001) and Wetland filtration (Kadlec and Knight, 1996).

The conventional technology for phosphate removal in industrial wastewater treatment consists of treating the wastewater with iron oxide tailing (chemical phosphate removal) (Zeng et al., 2004). In this process the phosphorus reacts with the iron to form iron phosphates which precipitate. A significant drawback of this process is the formation of large amount of sludge contaminated with metal salts. This sludge can only be disposed of by landfill, incineration or dumping at sea. To overcome secondary pollution problem various phosphate removal technologies were developed including adsorption. Adsorption is a versatile treatment practice widely used in process industries for wastewater treatment with operational simplicity and adsorbents' reuse potential separate it from the rest techniques. Activated carbon with porosity, internal surface area, relatively high mechanical strength and with very high removal efficiencies has proved to be the less expensive treatment option. Activated carbon mainly treats low concentration contaminants in wastewater streams to meet stringent treatment levels. For these reasons, activated carbon adsorption has been widely used for the treatment of wastewaters (Bansal and Goyal, 2005).

The rice husk and fruit juice residue are available in plenty without any cost in the market. Present study was undertaken to evaluate the efficacy of both adsorbents with and without activation under different operating conditions for the removal of phosphate from aqueous solutions. The novelty of the work is that both the phosphate loaded adsorbents after adsorption can be used as the feed-stock for biogas production using anaerobic digestion as phosphate is used as an essential inorganic nutrient for microbes during biomethanation process. Thus it eliminates the disposal problem of phosphate loaded adsorbents and also can be efficiently used for resource generation in terms of biogas production. Rice husk has been used for the first time as adsorbent for phosphate removal whereas fruit juice residue was never used as an adsorbent. Although phosphorous removal from secondary effluent using fruit juice residue was available in literature (Harada et al., 2011). Various adsorption isotherms, kinetics, thermodynamic studies and mass transfer mechanisms have been discussed in regard to phosphate removal from aqueous solution.

2. Materials and methods

2.1. *Adsorbents*

Rice husk (RH) and fruit juice residue (FJR) were used as low-cost natural biosorbents. Rice husk was collected from Banaras Hindu University farms and fruit juice residue (*Citrus limetta*) in solid form after extraction of juice collected from local fruit juice shop. The two adsorbents were thoroughly washed with double-distilled water to make the surface free of all the dust particles and muddy material adhered to it. Rice husk and fruit juice residue were dried at 105 °C for 24 h then grounded and used in the experiments.

The other two adsorbents namely activated rice husk (ARH) and activated fruit juice residue (AFJR) were prepared by activation of the above-mentioned adsorbents. It required washing of rice husk and fruit juice residue with double distilled water then they were submerged in 0.1 N NaOH followed by 0.1 N H_2SO_4 solution to remove the lignin based substances (Bhattacharya et al., 2008). Resulting masses were washed with double-distilled water and dried in sunlight for 12 h. There after oven-drying was carried out at 105 °C till a constant weight to make the surface ready and active for adsorption (Pradhan et al., 1998). The dried material was washed with 98% H_2SO_4 in the ratio of adsorbent to acid 1:1.5 by weight and cooled to room temperature with slow stirring. It was again washed with $NaHCO_3$ and double distilled water to remove acid traces. Finally it was dried in an oven and carbonized in muffle furnace in absence of air at 650 °C. Particles of the adsorbents were ground and sieved separately to different sizes and then stored in a vacuum desiccator for experimental purpose. The adsorbents having particle size of 250–350 μm were used for adsorption studies.

2.2. *Reagents*

The chemicals required for the analytical determination of phosphate in the aqueous solutions were potassium dihydrogen phosphate, ammonium molybdate, stannous chloride, glycerol, H_2SO_4. Hydrochloric acid and sodium hydroxide pellets were used for pH adjustment. All the chemicals were of analytical grade.

2.3. *Adsorbate solution*

The standard 50 mg/L phosphate stock solution was prepared by dissolving 219.5 mg of KH_2PO_4 in 1000 mL of distilled water. The stock solution was further diluted to have the required initial concentration of phosphate solutions.

2.4. *Instruments used*

Fourier transform infrared spectra of the samples was recorded by FTIR spectroscope (FTIR-8400, SHIMADZU) using KBr as reference. Digital pH meter (LI 120, Elico India) was used for measuring pH of the sample calibrated with standard buffer solutions (pH 4.0, 7.0 and 9.2). The Brunauer–Emmett–Teller (BET) surface area of the adsorbents were investigated by N_2 adsorption–desorption method using Micromeritics ASAP 2020, V302G single port. Liquid nitrogen was used as the cold bath (77 K). The porous structures were studied through BJH (Barret–Joyner–Halenda) data. The densities of the adsorbents were determined using specific gravity bottles. Elico SL 159 UV-VIS Spectrophotometer was used for obtaining concentrations of the phosphate solutions before and after adsorption to check the accurate phosphate removal.

2.5. *Batch adsorption techniques*

Adsorption tests were performed batch wise in 100 mL Erlenmeyer flask immersed in a temperature controlled water bath. Fixed amount of adsorbent was placed in a 100 mL flask containing aqueous solution of KH_2PO_4 used as phosphate source. The initial concentration was fixed at 10 mg/L for phosphate. After 3 h of vigorous stirring (180 rpm) at room temperature

Please cite this article in press as: Yadav, D., et al., Adsorptive removal of phosphate from aqueous solution using rice husk and fruit juice residue. Process Safety and Environmental Protection (2014), http://dx.doi.org/10.1016/j.psep.2014.09.005