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Modeling isotherms, kinetics and understanding the mechanism of phosphate adsorption onto a solid waste: Ground burnt patties

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ABSTRACT

The objective of the present study was to investigate the adsorption behavior of grounded burnt patties (GBP), a solid waste generated from cooking fuel used in earthen stoves, as an adsorbent for phosphate removal from aqueous solution. The characterization of adsorbent was done by proton induced X- ray emission (PIXE), and proton induced γ-ray emission (PIGE) methods and the adsorption mechanisms by Fourier transferred infra-red spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The effects of adsorbent dose, contact time, initial solution concentration, agitation, etc. on the uptake of phosphate by the adsorbent in batch mode were examined. The equilibrium data were fitted to different types of adsorption isotherms and kinetic models. Freundlich isotherm model and pseudo-second-order kinetic model illustrated best fit to the data. The favorability and spontaneity of the adsorption process are established by the values of experimentally calculated parameters such as separation factor (R_L), 0.03, Freundlich exponent (n), 3.57 and Gibb's free energy change (ΔG°), −1.32 kJ/mol. The presence of coexisting anions showed no competing effects on phosphate removal efficiency. Breakthrough curves obtained from column study revealed that the lower flow rate and higher bed heights result in longer column saturation time. The results of this study suggested that GBP can be used as a low cost, highly efficient adsorbent for phosphate removal from aqueous solution.

Introduction

Phosphorous is an essential element for the growth of microorganisms, plants and animals in most of the ecosystems, thus known as nutrient or biostimulant. Typically in aqueous environment, phosphorous exists in the form of orthophosphate, polyphosphates, pyrophosphate, organic phosphate esters and organic phosphonates, and all these forms could be hydrolyzed to orthophosphate and subsequently could be utilized by bacteria, algae, and plants. On the other hand, phosphorous is the limiting nutrient and sustained inputs of phosphorous (more than 1 mg/L) to aquatic environments lead to increased rates of eutrophication a widespread problem throughout the world affecting the quality of domestic, industrial, agricultural and recreational water resources [1,2]. Some of the ill effects of eutrophication include low dissolved oxygen, fish kills, murky water, and depletion of desirable flora and fauna [3]. In addition, the presence of nutrients in wastewater stimulates the activity of a harmful microbe known as *Pfisteria* and accelerate the production of microcystin, an environmental toxin that poison aquatic animals and can cause hepatocellular carcinoma in humans [4]. In order to prevent these problems phosphorous removal from wastewater is highly desirable before discharging. The World Health Organization (WHO) recommended a maximum discharge limit of phosphorous as 0.5–1.0 mg/L [5]. Therefore, in the current scenario, more and more stringent regulatory limits of phosphate discharge have been set by many nations and regions worldwide.

The primary input of phosphorous into the water bodies occurs by the discharge of municipal wastewater and industrial wastewater from detergent manufacturing and metal coating industries. Usually the concentration of phosphorous in municipal wastewater varies in the range of 3–15 mg/L, out of which approximately 3 mg/L forms by the breakdown of protein wastes and the remaining comes through the use of detergents [2]. Industrial wastewater may contain phosphorous in the concentration well in the excess of 10 mg/L [6]. So as to meet the effluent discharge standards, in many regions both municipal and industrial wastewater is treated before being discharged to the nearest watercourses. But the phosphorous concentration in the secondary effluents of treated municipal and industrial wastewater still remains more than 2 mg/L, which is well above the recommended maximum discharge limit of phosphorous by WHO. Therefore, secondary effluents containing substantial amounts of phosphorous needs to be treated effectively by other technologies. On-site systems using media filters have emerged as a promising solution for secondary effluent treatment and are of particular interest for

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Abbreviations: GBP, grounded burnt patties; PIXE, proton induced X-ray emission; PIGE, proton induced γ-ray emission; GBPT, grounded burnt patties treated; XRD, X-ray diffraction; FTIR, Fourier transferred infra-red spectroscopy; SEM, scanning electron microscopy; ZPC, zero point charge.

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nutrient removal [7]. The main mechanism of phosphorous removal in filter bed systems is generally through adsorption and precipitation within the filter material. Absorption is one of the promising approaches for the removal of phosphate and could be easily applied to small-scale treatment facilities or wastewater with relatively low phosphate concentrations without yielding harmful by-products [8]. The competency of the adsorption process depends upon the adsorbent materials, which should have certain advantages, such as low cost, easy availability and high uptake capacity [9]. Thus, at the time of designing on-site systems meant for phosphorous removal, appropriate selection of filter media (adsorbent) plays a vital role [10]. The most gainful materials are usually found among various waste materials, by-products and among natural minerals [11]. Till date diverse materials from industrial wastes including red mud, activated alumina, Fe, Al, Mg, Ca and Si based substrates, fly ash, blast furnace slag, etc., natural materials including various soils, laterite, dolomite, andesite, granite, etc., other waste materials including refuse concrete, waste paper, mussel shell, limestone waste, used bricks, etc., and from agricultural wastes including coir pith, date palm fiber, etc., have been reported as appropriate filter media that have been used to reduce phosphorous concentrations in the effluents efficiently [11–24].

Use of waste materials as adsorbents for phosphorous removal sounds promising. Moreover, exploiting the adsorption capacity of abundantly available local waste materials can be undoubtedly adjudged as the most cost-effective and environmental-friendly technology. By doing so either an increasing toxic threat to the environment can be prevented or waste disposal techniques can be streamlined making them more affordable. This study is thus relevant as it involves the evaluation of phosphate adsorption capacity of burnt patties, a solid waste generated after burning patties in earthen cooking stoves or chullahs in households for cooking. Generally patties are prepared by mixing coal dust or coal cinder with a definite proportion of soil and cow dung and by drying them in the sun before use. Coal cinder is burnt or partly burnt coal, which is not reduced to ash and that can burn further but without flame. In city slums and rural areas of developing countries like India, the majority of the populations are not able to get cooking gas and electricity supply. The other sources of fuel such as wood and coal are in difficult supply due to depletion of plant biomass. Petroleum products such as kerosene are in short supply and the price is unaffordable. Therefore, the remaining alternative of fuel source for rural masses is cow dung cakes and for city masses is patties. Moreover, restricting the use of LPG (liquefied petroleum gas) cylinder by India government is compelling small food stalls, dhabas and hotels of city areas to switch over to patties as a source of cooking fuel. Increased use of the patties leads to the generation of a large amount of solid wastes which are casually dumped triggering environmental and hygiene problems such as mosquito breeding. On the other hand the patties are rich in aluminum, iron, calcium and magnesium and these compositions add to the possibility of patties to be used as a phosphorous adsorbent. Exploring phosphorous removal ability of patties can address two major issues such as the phosphorous removal and waste recycling.

The main objective of this study was to inspect the use of grounded burnt patties (GBP) as an adsorbent for the adsorption of phosphorous. Surface characteristics and physico-chemical properties of the patties have been investigated. Kinetic and isotherm models have been analyzed and presented to envisage the phosphorous sorption characteristics of the patties. Although very few literatures have been observed to report phosphorous adsorptive behavior of coal cinder, so far, to the best of our knowledge, no study has been reported to evaluate the phosphorous adsorption potential of GBP.

Table 1
Properties and compositions of grounded burnt patties (GBP).

Properties and compositions	Grounded burnt patties (GBP)
Particle size (mm)	<0.3
pH_{zpc}	8.62
BET surface area (m^2/g)	19.07
Bulk density (g/cm^3)	2.0
Porosity (%)	74.48
Specific gravity	2.41
Specific yield (%)	62.19
Specific retention (%)	12.29
SiO_2 (%)	52.71–54.49
Fe_2O_3 (%)	17.95–18.72
Al_2O_3 (%)	20.74–21.42
MgO (%)	4.85–5.01
Na_2O (%)	0.37–0.40
CaO (%)	3.8–4.11

Materials and methods

Adsorbent

Burnt patties were collected from different waste disposal sites of Bhubaneswar city, Odisha, India. The collected patties are grounded, sieved, washed several times with distilled water to remove surface adhered particles and soluble materials, and dried in hot-air oven at 100 ºC for overnight. The grounded burnt patties (GBP) of particle size less than 0.3 mm were used in the adsorption study. The properties and average chemical composition of the material were given in Table 1. For the composition analysis of GBP, highly sensitive multi-component analytical methods like proton induced X- ray emission (PIXE) and proton induced γ-ray emission (PIGE) were used.

Aqueous solution of phosphate

Synthetic phosphate stock solutions of 1000 mg/L were prepared by dissolving defined amount of analytical grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) in distilled water. The stock solution was further diluted with distilled water to get the desired concentrations of experimental working solution. This synthetic phosphate solution was used for optimizing different adsorption parameters in both batch and column studies.

Analytical methods

The chemical compositions of GBP were analyzed with the help of proton induced X- ray emission (PIXE) and proton induced γ-ray emission (PIGE). Measurements were carried out using the 2 MeV proton beam obtained from 3 MV tandem pelletron accelerator. In order to get better resolution and clarity of results, PIXE was done for the analysis of elements with atomic number as low as 12 (low Z elements) and PIGE was done for the analysis of high Z elements following the method as described by Kennedy et al. [25].

The adsorbents before adsorption and after adsorption were termed as GBP and GBPT, respectively, and were characterized by Fourier transferred infra-red spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The FTIR spectra were recorded on Bruker ALPHA-FTIR Spectrophotometer. Samples were prepared in KBr disks (2 mg sample in 200 mg KBr). The scanning range was 500–4000 cm^{-1} and the resolution was 2 cm^{-1} with a scanning rate of 16. The XRD analysis was performed in an X'pert PW 3040/00 (PANalytical) diffractometer at room temperature, with Cu Kα radiation at a scan speed range of 3°/min, step size of 1 s, 30 kV voltage and 20 mA current. The XRD patterns were recorded in the 2θ