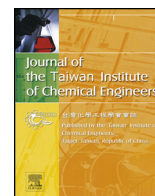




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Effective utilization of a sponge iron industry by-product for phosphate removal from aqueous solution: A statistical and kinetic modelling approach

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ABSTRACT

Dolochar, a solid waste generated from sponge iron industry during the process of direct reduction of iron by rotary kiln, is explored as an adsorbent for phosphate removal in this study. The depiction of the adsorption process was done by X-ray diffraction (XRD), Fourier transferred infra-red spectroscopy (FTIR), and Energy dispersive spectroscopy (EDS) analysis. The appearance of phosphorous peak in EDS spectra of spent dolochar confirmed phosphate adsorption. Application of response surface methodology (RSM) and analysis of variance (ANOVA) for modelling and optimization of phosphate removal in batch study and breakthrough time in column study, suggested quadratic models for both the responses. Experimental validation of the optimization process resulted in 98.13% phosphate removal and 24.67 h breakthrough time. Pseudo second order kinetic and Langmuir isotherm illustrated best fit to the experimental data with $R^2 = 0.98$ and $R^2 = 0.99$, respectively. The values of separation factor ($1 > R_L > 0$), Freundlich exponent ($n > 1$) and thermodynamic parameters (ΔG° , -3442.6 kJ/mol and ΔH° , 6627 kJ/mol) specified favourable spontaneous and endothermic adsorption process. The adsorbent displayed 80% of the original adsorption capacity in the 3rd cycle of reuse. The results of this study support the utility of dolochar as a low cost and highly efficient adsorbent for phosphate removal from aqueous solution.

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1. Introduction

Dolochar is a by-product of sponge iron industry. Sponge iron is produced from the ingredients like iron ore, dolomite and coal with the application of direct reduction of iron (DRI) methodology. The waste material generated during the DRI process, consisting of devolatilized dolomite and char (the solid remnant of coal after the release of coal gas and coal tar during the initial stage of combustion) is termed as dolochar. A typical sponge iron industry (using DRI methodology) with 100 t per day capacity produces 25 t per day dolochar, thereby generating 9000 t waste material per annum [1,2]. A negligible portion of the generated dolochar is used as domestic fuel, fuel in boilers and brick making industries, whereas the major portion is either dumped in the dump yards or is used in the land filling without considering their effect in aquatic and edaphic environments. Therefore, the utility of such large

amount of dolochar generated still appears to be an unanswered predicament, and hence, threat the environment with serious disposal problems. In order to find some utility of dolochar, the adsorption potential of the same was explored by Panda et al. [1] to remove heavy metals like Cd(II) and Cr(VI). The most prolific adsorbents are usually found among various industrial waste materials [3]. The innate porosity and the presence of iron, aluminium, calcium and magnesium compounds in dolochar add to the possible application of the waste for phosphate adsorption. There are well documented literatures available suggesting that, phosphate ions react with iron and aluminium oxides by ligand exchange forming inner-sphere complexes whereas the presence of magnesium and calcium ion facilitates phosphate removal via precipitation [4–6]. Owing to the above facts, examination of phosphate adsorption potential of dolochar has been attempted in this study.

Phosphate is an indispensable macronutrient for the growth, development and normal functioning of biological organisms in most of the ecosystems [7]. Conversely, with rapid industrialization and urbanization, the excess discharge of phosphates to

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aquatic environments is taking place through various anthropogenic activities such as the use of fertilizers, pigments, detergents and electronic industry discharge, domestic wastewater discharge, mineral processing, rural and urban sewage disposal *etc.* [8]. Apart from eutrophication, the increasing loads of phosphates in water bodies stimulate the activity of a damaging microbe known as *Pfisteria* and speed up the production of microcystin, a toxin that poisons aquatic animals and can cause hepatocellular carcinoma in humans [9] and [10]. As per USEPA report [11], dissolved phosphate concentration of 0.02 mg/L is considered to have potential eutrophic effects in aquatic bodies. To meet the stringent limit of phosphorous concentration in natural water bodies, the discharge standard of wastewater is on an average set at 1–2 mg/L of phosphate [12]. In recent past, a great deal of advanced treatment methods such as physical processes, chemical precipitation, biological treatment and adsorption based processes *etc.* have been practised for phosphate abatement, since phosphate is usually difficult to remove by conventional wastewater treatment plants [13], [14,15]. Among the easily reached processes, adsorption comes into sight to be more efficient and economical with advantageous features like, low operational cost, less production of sludge and fewer disposal problems *etc.* In addition, the phosphate loaded adsorbents can be also used in agricultural sector as fertilizer and soil conditioner [16]. Till date, the application of various adept solid materials as adsorbents, involving synthetic materials [8–18], natural materials [9,13,19–21], agricultural by-products [22,23] and industrial by-products [7,24–26], in phosphate removal from aqueous solutions have been extensively looked over.

Prediction of the effects of multiple parameters and their interaction is difficult through conventional experimental methodologies which are based on one-variable-at-a-time (OVAT). Also by considering more experimental parameters for a particular process, more number of experiments will have to be performed, which is cumbersome and time consuming [27]. Response surface methodology (RSM) has been attested to be a handy tool for fulfilling the purpose of studying the effects of multiple parameters simultaneously, while performing a reduced number of experiments [28]. RSM has been applied to optimize and model phosphate adsorption onto hydrated ferric oxide-based nanocomposite, powder alum sludge, NF90 membrane *etc.* [18,27,29]; however, no such report is found on the application of RSM to optimize phosphate removal from aqueous solution using dolochar as an adsorbent. Therefore, the multi fold objective of this study includes (i) investigation of the phosphate removal ability of dolochar, from aqueous solution, both in batch and column mode of operation, (ii) characterization of adsorbent and adsorption process with the help of XRD, FTIR and EDS, (iii) application of RSM to optimize experimental parameters and to develop statistical models of adsorption both in batch and column mode, (iv) determination of adsorption mechanism, kinetics, thermodynamics, isotherms, adsorption–desorption cycle *etc.* In short, an economic, easy and eco-friendly phosphate removal method has been attempted, especially, emphasizing on bulk utilization of dolochar, thereby making light of disposal issues.

2. Materials and methods

2.1. Adsorbent

Dolochar samples were collected from three sponge iron industries located in Sambalpur and Anugul district of Odisha, India. The collected samples were grounded, sieved and washed several times with distilled water to remove surface adhered particles, soluble materials and then dried in hot-air oven at 100 °C for overnight. Dolochar sample of particle size less than 0.6 mm

Table 1
Properties and compositions of dolochar.

Properties and compositions	Dolochar
Particle size (mm)	<0.6
pH _{zpc}	11.22
BET Surface area (m ² /g)	104.31
SiO ₂ (%)	53.67 ± 3.23
Al ₂ O ₃ (%)	18.39 ± 1.38
Fe ₂ O ₃ (%)	16.72 ± 1.67
MgO (%)	5.09 ± 0.96
CaO (%)	4.23 ± 0.58

were used in the adsorption study. The properties and average chemical composition of the material are given in Table 1. The chemical compositions of the dolochar samples were analyzed by wet chemical and atomic absorption spectrophotometer (AAS) techniques.

2.2. Adsorbate

Chemicals of analytical grade used in the present experimental studies, were procured from Himedia Laboratories Pvt. Ltd. Mumbai, India. Phosphate stock solutions of 1000 mg/L were prepared synthetically by dissolving calculated amount of anhydrous potassium dihydrogen phosphate (KH₂PO₄) in distilled water. The stock solution was further diluted 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. The pH of the phosphate solution was adjusted to desired value by addition of 0.1 M HCl and NaOH.

2.3. Analytical methods, related instruments and software

Phosphate concentration in aqueous solutions was determined by the vanado molybdo phosphoric acid method [30]. 1 mL of vanadate-molybdate reagent, 0.5 mL of distilled water and 3.5 mL of filtered sample were mixed and the solution was analyzed after 10 min with a UV/VIS spectrophotometer (Perkin Elmer Lambda-25) at the detection wavelength of 470 nm. The XRD analysis was carried out in the 2 θ range of 15–70° in a Bruker D8 DISCOVER diffractometer at room temperature, with Cu K α radiation operated at 40 kV voltage, 40 mAmp current, scan speed of 3°/min and step size of 1 s. The FTIR spectra of KBr disks containing adsorbent sample (2 mg sample in 200 mg KBr) were recorded on Bruker ALPHA-FTIR Spectrophotometer by setting the scanning range of 500–4000 cm⁻¹, resolution of 4 cm⁻¹ and a scanning rate of 64. Elemental distribution of dolochar before and after adsorption was monitored using field emission scanning electron microscope (FESEM, ZEISS SUPRA 55), equipped with EDS at an accelerating voltage of 15 kV by sprinkling adsorbents onto the carbon tape mounted on the SEM stub. To determine pH_{zpc}, 1 g of dolochar was added to a series of Elnermayer flasks containing 100 mL of 0.01 M NaCl solution of variably adjusted pH (2.5–12), agitated for 48 h and then final pH was measured. The pH_{zpc} was obtained as the point of intersection (pH = 0) of the resulting curve as obtained by plotting change in pH (Δ pH) against the initial pH (pH_i). The specific surface area of dolochar was determined by the BET nitrogen gas adsorption–desorption method using a specific surface area analyzer, QUADRASORB SI, USA.

Design Expert version 7.0.3, Stat Ease, USA was used for the application of RSM to fit and analyze experimental data to various models. Statistical validation of the models was done by analysis of variance (ANOVA). XRD data were analyzed by DIFRAC.SUITE XRD software, FTIR data by e-FTIR software, and BET analysis by Quadra Win software.

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