Contents lists available at ScienceDirect

Process Safety and Environmental Protection

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

Nutrient removal from binary aqueous phase by dolochar: Highlighting optimization, single and binary adsorption isotherms and nutrient release

Prangya Ranjan Rout, Rajesh Roshan Dash, Puspendu Bhunia *

School of Infrastructure, Indian Institute of Technology Bhubaneswar, Bhubaneswar 751 013, Odisha, India

ARTICLE INFO

Article history:
Received 5 October 2015
Received in revised form 4 December 2015
Accepted 4 January 2016
Available online 9 January 2016

Keywords:
Dolochar
Nutrient removal
Binary adsorption system
Response surface methodology
Multicomponent isotherms
Slow release of nutrient

ABSTRACT

The viability of utilizing sponge iron industry based waste 'dolochar' as a proficient adsorbent for nutrient (phosphate and nitrate) removal and subsequent slow release of nutrient from the spent dolochar has been undertaken in this study. The efficacy of dolochar has been explored in both single and binary adsorption systems containing nutrients. The proposed experimentally obtained quadratic models for both the phosphate and nitrate removal were substantiated by analysis of variance (ANOVA) with high R^2 values of 0.99 and 0.98, respectively. Response surface methodology (RSM) based optimization followed by experimental validation resulted in phosphate removal efficiency of 96.7% and nitrate removal efficiency of 57.1%. Single component adsorption equilibrium data fitted well to pseudo-second order kinetic and Langmuir isotherm models with Langmuir maximum adsorption capacity, q_m of 327.7 and 6.51 mg g^{-1} for phosphate and nitrate, respectively. Out of non-modified Langmuir, modified Langmuir, extended Langmuir and extended Freundlich, multi component isotherm models, binary adsorption equilibrium data fitted well to the extended Freundlich model. Thin layer funnel analytical test results reveals the slow nutrient release nature of spent dolochar. The results suggest that the dolochar has the potential to serve as a sustainable adsorbent for nutrient removal from wastewater along with the scope of utilizing spent dolochar as a slow release nutrient supplier.

1. Introduction

Nutrient over loading in sensitive ecosystems for the most part, was induced by industrial discharges (detergent manufacturing, mineral processing, thermal power plants etc.) over application of synthetic and natural fertilizers in agricultural sectors, aquaculture, municipal wastewaters, household wastes and many other human activities (Olgun et al., 2013; Saad et al., 2007). Lots of aquatic ecosystems have awfully low ambient nutrient concentrations and a small shift in the nutrient load can result in striking changes in community structure (Dodds and Welch, 2000). Persistent inputs of nutrients (phosphate more than 0.5–1 mg L^{-1} and nitrate more than 45 mg L^{-1}) to aquatic environments lead to increased rates of eutrophication hence deteriorate the water quality, a global widespread problem in recent times (World Health Organization, 1998; Sowmya and Meenakshi, 2013). Moreover, existence of nutrients in wastewater stimulate the activity of a harmful microbe known as *Pfisteria* and speed up the production of microsystin, a toxin that poison aquatic animals and can cause hepatocellular carcinoma in humans (Yuan et al., 2006). Also excess nitrate nitrogen in drinking water may contribute to a serious illness in infants called methemoglobinemia or "blue baby syndrome", miscarriages in case of pregnant women, acute poisoning in cattle and the formation of nitrosoamines and nitrosoamides, which are related

* *Corresponding author.* Tel.: +91 674 2306355; fax: +91 674 2301983.
E-mail address: pbhunia@iitbbs.ac.in (P. Bhunia) .

http://dx.doi.org/10.1016/j.psep.2016.01.001
0957-5820/

to cancer (Hamoudi et al., 2007; Pontius and Association, 1990; Romano and Zeng, 2009). In a nutshell, the undesirable impacts of nutrient overloading are becoming progressively more visible in the form of reduced biodiversity of aquatic species, impairment of human health, reduction in amenity value, and increased costs of treatment for drinking water. Thus, improvement of wastewater treatment methods that make possible the removal of nutrients prior to discharge into aquatic environments, is highly essential (Withers et al., 2009; Xu et al., 2010).

Till date, several methods have been explored for the removal of dissolved nutrients from water and wastewater, which are roughly classified as biological (Bassin et al., 2012), physicochemical such as ion exchange, adsorption, electro coagulation etc. (İrdemez et al., 2006; Taleb et al., 2008; Xu et al., 2010) and physical methods like electro dialysis, reverse osmosis etc. (Altundoğan and Tümen, 2002). Among the accessible processes, adsorption appears to be more efficient and economical with advantageous features like, easy handling, low operational cost, less production of sludge, fewer disposal problems and it allows the use of easily accessible low cost materials as adsorbents. In addition, the nutrient loaded adsorbents can be also used in agricultural sector as fertilizer and soil conditioner (Hylander et al., 2006). The success of the adsorption process depends mostly upon the choice of adsorbent materials, which should have the properties of low cost, easy availability and high uptake capacity. The most productive materials are usually found among various industrial by-products, waste materials and among natural materials (Mateus et al., 2012). The application of proficient solid materials as adsorbents, involving synthetic materials (Bolan et al., 2004; Halajnia et al., 2013; Hamoudi and Belkacemi, 2013; Jiang et al., 2013; Sowmya and Meenakshi, 2013; Taleb et al., 2008; Yadav et al., 2015), natural materials (Akosman and Özdemir, 2010; Hamoudi et al., 2007; Kilpimaa et al., 2015; Rout et al., 2014, 2015b; Routa et al., 2014; Saad et al., 2008), agricultural by-products (Hale et al., 2013; Namasivayam and Höll, 2005; Namasivayam et al., 2007; Xu et al., 2010) and industrial by-products (Ji et al., 2015; Olgun et al., 2013; Wendling et al., 2013), in nutrient removal from aqueous solutions has been widely inspected in recent times.

Of late, substantial experimental advancements have been made in the use of dolochar, a sponge iron industry waste for the removal of heavy metals like Cd(II) and Cr(VI) (Panda et al., 2011) from aqueous solutions. The throw away matter produced during the direct reduced iron (DRI) process, consisting of dolomite and char is termed as dolochar (Botha, 1993). A representative sponge iron industry with 100 tons (t) per day capacity produces 25 t per day dolochar, thereby, producing 9000 t waste material per annum (Dwari et al., 2012; Panda et al., 2011). Such a huge quantity of dolochar generated emerges as a threat to the environment with serious disposal issues. On the other hand, dolochar is a carbonaceous substance being subjected to high temperature treatment during DRI. This condition enables dolochar to have high surface area and inherent porosity, similar to activated carbon and probably can be used as an adsorbent. So as to establish the utilization of dolochar as an adsorbent, nutrient adsorption study has been attempted in this work.

The individual adsorption of nitrate and phosphate from aqueous solution on various adsorbents has been extensively studied. However, real wastewater normally contains both nitrate and phosphate ions. In an attempt to find out the affinity of each species toward the adsorbent (dolochar) and to know if there is competition among the two species for the same adsorption sites, the bi-component adsorption of nutrients from binary solution has been undertaken. Moreover, response surface methodology (RSM) has been applied to optimize and model nutrient adsorption onto dolochar. This also facilitates investigation of the simultaneous effects of multiple parameters on adsorption process by performing less number of experiments (Box and Draper, 1987). The many fold objectives of this study embrace (i) exploration of the single and binary adsorption of nutrient on dolochar from aqueous solution, (ii) RSM based optimization of experimental parameters and development of statistical models for adsorption process, (iii) modeling of the adsorption equilibrium data with the single and binary adsorption isotherms and (iv) determination of adsorption mechanisms and kinetics and (v) establishing the applicability of the spent adsorbent as a nutrient supplier. To be brief, an economic, easy and eco-friendly nutrient removal process has been attempted, particularly, emphasizing on bulk utilization of dolochar.

2. Materials and methods

2.1. *Preparation of dolochar*

Dolochar samples were collected from different sponge iron industries situated in Odisha, India. The collected samples were subjected to grinding, sieving, followed by washing several times with distilled water to remove surface adhered particles, soluble materials and then dried in hot-air oven at 100 °C for overnight. Particle sizes less than 0.6 mm of the adsorbent materials were used in the adsorption study.

2.2. *Preparation of nutrient solutions*

Phosphate and nitrate stock solutions of 1000 mg L^{-1} were prepared by dissolving calculated amount of anhydrous KH_2PO_4 and KNO_3 in distilled water. The stock solution was further diluted to get the desired concentrations of experimental working solution. The pH of the working solution was adjusted to the desired value by the addition of 0.1 M HCl and NaOH. All the chemicals used in this study were of analytical grades and procured from Merck, Mumbai.

2.3. *Characterization of dolochar and analytical methods*

The mineral composition of the dolochar was analyzed by proton induced X-ray emission (PIXE) and proton induced γ-ray emission (PIGE), using the 2 MeV proton beam obtained from 3 MV tandem pelletron accelerator, following slightly modified procedure as described by Kennedy et al. (1999). The XRD analysis was done in the 2θ range of 15–70° in Bruker D8 DISCOVER diffractometer at room temperature, with Cu $K\alpha$ radiation operated at 40 kV, 40 mAmp with a scan speed of 3° min^{-1}. KBr disks containing adsorbent (2 mg dolochar in 200 mg KBr) were prepared and the FTIR spectra were obtained from Bruker ALPHA-FTIR Spectrophotometer by averaging 64 scans from 500 to 4000 cm^{-1}, at a resolution of 4 cm^{-1}. Elemental distribution of dolochar was monitored using Field Emission Scanning Electron Microscope (FESEM, ZEISS SUPRA 55), equipped with EDS at an accelerating voltage of 15 kV. 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. So as to measure pHzpc, 1 g of