Ecological Engineering 97 (2016) 13–22

Contents lists available at ScienceDirect

Ecological Engineering

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

Sun coral powder as adsorbent: Evaluation of phosphorus removal in synthetic and real wastewater

Marco Tadeu Gomes Vianna[a,*], Marcia Marques[a,b], Luiz Carlos Bertolino[c]

[a] Department of Sanitary and Environmental Engineering, Rio de Janeiro State University, Brazil
[b] Department of Biology and Environ. Science, Linnaeus University, 391 82 Kalmar, Sweden
[c] Centro de Tecnologia Mineral – CETEM, CNPq, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

Article history:
Received 15 March 2016
Received in revised form 21 June 2016
Accepted 4 August 2016

Keywords:
Phosphorus removal
Wastewater
Sorption processes
Factorial design
Response surface methodology
Sun coral

ABSTRACT

Two exotic species introduced during the 90 s known as sun coral currently spread along 2000 km of the Brazilian coast pose a severe threat to the marine biodiversity. Since they have exoskeletons with high concentration of calcium carbonate, the present investigation focused on the removal of phosphorus from wastewater, using exoskeleton's powder in three forms: raw (RSC); physically modified (SCA) and chemically modified (SCC). A Central Composite Design with Response Surface Methodology was applied to the assays along to studies of kinetics, thermodynamics and equilibrium and sorbent's characterisation by FTIR, XRD and SEM-EDX techniques. The maximum P removal capacities of RSC, SCA and SCC were 6826, 7062 and 9597 mg P kg^{-1}, respectively. In all cases, the adsorption followed the Langmuir's pseudo-second-order kinetic model being the process thermodynamically appropriate. The sun coral-based adsorbent is an attractive option for wastewater treatment and may contribute to the control of the sun coral population.

1. Introduction

Phosphorus can be present in the following forms in the water and wastewaters: (i) organic form bound to organic compounds originated from physiological processes; (ii) inorganic polyphosphates and orthophosphates, originated mostly from detergents and other household products and; (ii) in organic form bound to organic compounds originated from physiological processes. The form in which orthophosphate is found in water (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$ or H_3PO_4) depends on the pH. In a typical wastewater, the predominant form is HPO_4^{2-} (Mangwandi et al., 2014). Polyphosphates and organic phosphorous are converted into orthophosphate by hydrolysis/or microbial mobilization. The concentration of phosphates in the Brazilian raw sewage, for instance, ranges from 5 to 8 mg L^{-1}.

The most commonly used method for phosphorus removal from wastewater is chemical precipitation and this method can reduce the concentration of phosphorus to values below 1 mg L^{-1} in sewage treatment plants. However, chemical precipitation is expensive for many parts of the world; can produce new pollutants such as chloride and sulphate (Altundogan and Tumen, 2002); demands destination/disposal for the precipitate obtained and neutralization of the treated effluent. In addition, the method is unsuitable for treating effluents containing ions in low concentrations. Alternative methods for phosphorus removal include biological treatment, constructed wetlands (Salomão et al., 2012), electro-dialysis, reverse osmosis, ultrafiltration and adsorption. Among them, adsorption seems to be an effective treatment option because of convenience, ease of operation, simplicity of design and economic point of view. Adsorption used as treatment generate spent/used adsorbent that can be used, for instance, for soil amendment such as pH correction and as fertilizer (Karageorgiou et al., 2007); additionally, it is worth to mention the possibility of regenerating adsorbents for reuse.

Natural materials such as apatite, bauxite, limestone, sand, shells, among others, have been used as adsorbents for removal of phosphates from water (Vohla et al., 2011). Metal oxides and hydroxides (Genz et al., 2004), layered double hydroxides (LDH) (Das et al., 2006), developed material (Adam et al., 2005; Gustafsson et al., 2008; Kumar et al., 2014; Öövel et al., 2007) and agro-industrial wastes have also been used (Bhatnagar and Sillanpää, 2010; Bhatnagar et al., 2014; Wen et al., 2015). These materials can be used in selective reactors in systems built in bench and real scales (Kwon et al., 2004; Li et al., 2006). In common, these materials have high concentration of calcium (Ca), iron (Fe) and

* Corresponding author.
E-mail addresses: tadeu_vianna@hotmail.com, tadeu_vianna@superig.com.br (M.T.G. Vianna).

http://dx.doi.org/10.1016/j.ecoleng.2016.08.004
0925-8574/

Fig. 1. (a) Sun coral in Ilha Grande Bay (Photo by Joel Creed/Projeto Coral-Sol/BrBio). (b) Sun coral occupation along the Brazilian coastline during the 80–90's (yellow line) and in 2015 (red line) (map modified from Google Earth). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aluminium (Al) in their structures with high yield for phosphorus removal, through adsorption or precipitation processes. Some of these materials, show high performance for orthophosphate's removal and saturation is achieved only after years of use, which make them a sustainable solution (Brix et al., 2001).

1.1. *The sun coral problem in the Brazilian coast*

The introduction of exotic species in aquatic environments has long been considered an environmental problem that affects the integrity of natural communities, mechanisms such as competition, predation and parasitism, and alters food webs and nutrient cycles (Bax et al., 2003). Some of these invasive species have high concentrations of calcium in their exoskeleton composition, potentially useful in water treatment, particularly for phosphorus removal.

Sun coral (Fig. 1) refers to two species (*Tubastraea coccinea* and *Tubastraea tagusensis*, Scleractinia order, Dendrophylliidae family) native from Asia and very abundant in the Indian and Pacific oceans (Cairns, 2015). However, the sun corals are invasive species that rapidly colonizes large areas, in recent decades, its range distribution has increased, and today, the species is considered pantropical, being observed in Caribbean Sea (Puerto Rico and Curaçao), Gulf of Mexico (including the Flower Garden Banks Marine Sanctuary and Florida Keys) and Western Atlantic (Brazilian Coast) (Sammarco et al., 2013).

In Brazilian Coast, sun coral was first observed the 1980s, in an oil and gas platform in Campos Basin, Northern of Rio de Janeiro state (Fig. S1) (Castro and Pires, 2001). During the 1990s, the species were reported in Ilha Grande Bay, South of Rio de Janeiro State (Paula and Creed, 2005). Currently, the sun coral's occupation extends over 2000 km of the Brazilian coast (Fig. 1, S1 and S2) and at least 20 oil platforms, ships and nautical monobuoys (Mantelatto et al., 2011; Silva et al., 2014). These corals are opportunistic species with high production of oocytes, early childbearing age, short time incubation embryo and hermaphroditism (Creed and De Paula, 2007). Sun coral produces substances with anti-fouling and anti-predatory properties and releases allelopathic substances that cause necrosis to Brazilian endemic species (Lages et al., 2010) posing serious threat to the Brazilian marine biodiversity and affect species economically important.

During recent years, the Federal Public Ministry has moved civil actions in different Brazilian states, requesting an injunction to protect the marine environment and control sun coral expansion. Since sun coral incrustation causes damage to oil platforms, their removal has been necessary as part of platforms maintenance. Currently, attempts to control the expansion of sun coral infestation include manual and mechanical removal and inoculation by specific bacteria and viruses. One strategy to promote the removal of these species would be to assign use to the extracted material, making the extraction economically attractive.

This study aims to investigate the capacity of exoskeleton (in powder form) of sun coral in removing orthophosphates from synthetic and real wastewaters. The investigation compared the raw (RSC), with physically (SCA) and chemically (SCC) modified material. The performance of these adsorbents regarding phosphorus removal from wastewater was assessed using design of experiments (DoE) principles for process optimization, associated to studies of kinetics, thermodynamics and equilibrium in the best configurations obtained with the Central Composite Design (CCD) for each material.

2. Material and methods

2.1. *Experimental planning*

2.1.1. *Materials*

All chemicals were purchased from Sigma-Aldrich and all solution were prepared using deionized Milli-Q water (Millipore TM – resistivity of ≥18.2 MW cm^{-2}). The phosphorus solution was prepared by dissolving the primary standard potassium dihydrogen phosphate (KH_2PO_4) in Milli-Q water. The stock solution was prepared with 100 mg L^{-1} of P and diluted properly for use according to the predicted by CCD levels (see concentrations of P in Table S1). For pH adjustment, solutions of 0.1 N sodium hydroxide (NaOH) and 0.1 N hydrochloric acid (HCl) and a multiparameter 5 Star Orion (Method: 4500H + B) were used (Eaton et al., 2005).

2.1.2. *Preparation of sun coral powder*

The sun coral was obtained from Ilha Grande Bay, Rio de Janeiro, Brazil. The material collected was dehydrated in an oven at 60 °C during 72 h. The sun coral exoskeleton was then, washed at room temperature to remove the remaining impurities. Subsequently, the exoskeleton was submerged in vessels containing sodium hypochlorite 10% (NaClO-10% w/v) and at this stage, the exoskele-