Journal of Environmental Management xxx (2017) 1–8

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Manufacturing of novel low-cost adsorbent: Co-granulation of limestone and coffee waste

Evgenia Iakovleva [a, b, *], Mika Sillanpää [a, c], Philipp Maydannik [a], Jiang Tao Liu [b], Stephen Allen [b], Ahmad B. Albadarin [b, d], Chirangano Mangwandi [b]

[a] Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130, Mikkeli, Finland
[b] School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, Northern Ireland, UK
[c] Department of Civil and Environmental Engineering, Florida International University, 10555, West Flagler Street, Miami, FL, 33174, USA
[d] School of Natural Sciences, Bernal Institute, University of Limerick, Limerick, Ireland

A R T I C L E I N F O

Article history:
Received 7 April 2016
Received in revised form
2 May 2017
Accepted 10 May 2017
Available online xxx

Keywords:
Wet granulation
Bio-waste
Methylene blue
Orange II

A B S T R A C T

Limestone and coffee waste were used during the wet co-granulation process for the production of efficient adsorbents to be used in the removal of anionic and cationic dyes. The adsorbents were characterized using different analytical techniques such as XRD, SEM, FTIR, organic elemental analysis, the nitrogen adsorption method, with wettability, strength and adsorption tests. The adsorption capacity of granules was determined by removal of methylene blue (MB) and orange II (OR) from single and mixed solutions. In the mixed solution, co-granules removed 100% of MB and 85% of OR. The equilibria were established after 6 and 480 h for MB and OR, respectively.

1. Introduction

During recent decades, researches considered solid wastes as sources of biofuels (Schröder, 2015), fertilizers (Nishio and Nakashimada, 2013), composite materials (Pavla, 2011) and low-cost adsorbents for water treatment (Kaushik et al., 2009; Bhatnagar et al., 2015; Iakovleva and Sillanpää, 2013). The main problems regarding water treatment are the minimization and reuse of processed water, and cost saving including a reduction in energy consumption. Despite a quarter century of studies, these problems of solid and liquid wastes management are as relevant today as 25 years ago, when the term "industrial ecology" was introduced (Smith et al., 2015).

For example, Finland is first in the world for coffee consumption and has about 50M kg coffee wastes per year (Ojaniemi, 2010). Coffee wastes are mostly used as a source for bio-energy and fertilizers (Cruz et al., 2015; Adi and Noor, 2009). In some research papers, coffee waste has been used as biosorbents for the removal of acid dye (Gupta and Suhas, 2009; Rafatullah et al., 2010; Lafi et al., 2014; Roh et al., 2012; Kyzas et al., 2012), organics (Al-Zaben and Mekhamer, 2013; Lafi and Hafiane, 2015; Rossmann et al., 2012) and metal ions from aqueous solutions (Azouaou et al., 2010; Boonamnuayvitaya et al., 2004; Ching et al., 2011; Kaikake et al., 2007; Oliveira et al., 2008; Pujol et al., 2013). Coffee waste has a high C/N ratio, and contains carboxylic group (Cruz et al., 2015) ensuring high efficiency for metal ions removal due to chelates formation (Adi and Noor, 2009; Lafi et al., 2014). Therefore, the coffee waste could be used as potentially effective sorbent for various pollutants, including metal ions. In order to test properties of new adsorbent Methylene Blue (MB) and Orange II (OR) were used as model acidic and basic pollutants, respectively. Various functional groups such as amino, hydroxyl, carboxyl and sulfate on the bio-waste surface, which can act as binding sites for acidic and basic dyes, help to increase the adsorption effect (Adegoke and Bello, 2015; Kyzas et al., 2012). Clay and siliceous materials show high affinity for pollutants in acidic solution as a scavenger through an ion-exchange process (Iakovleva et al., 2015).

A combination of limestone and coffee waste might improve the removal efficiency of pollutants and ensure neutralization of the acidic water, based on the ion-exchange reactions on the surface of combined sorbent.

* Corresponding author. Laboratory of Green Chemistry, School of Engineering Science, Lappeenranta University of Technology, Sammonkatu 12, FI-50130, Mikkeli, Finland.
E-mail address: evgenia.iakovleva@lut.fi (E. Iakovleva).

http://dx.doi.org/10.1016/j.jenvman.2017.05.039
0301-4797/© 2017 Published by Elsevier Ltd.

Please cite this article in press as: Iakovleva, E., et al., Manufacturing of novel low-cost adsorbent: Co-granulation of limestone and coffee waste, Journal of Environmental Management (2017), http://dx.doi.org/10.1016/j.jenvman.2017.05.039

Adsorbents must have certain properties to be suitable for industrial use. The combined sorbents must be resistant to water, must not stick together, and should retain the properties of the original materials (Albadarin et al., 2014; Mangwandi et al., 2014). Granulation of two different materials was chosen as a way to produce a uniform dual adsorbent. There are some requirements of the material to be produced, including segregation of the powder particles, uniform granules, their wettability, strength and stability in the solutions. The adsorbent should be stable to the transportation as well. The main parameters of the granulation process are process variables such as processing time, impeller speed and formulation variables such as particles size and choice of binder. Homogeneous materials are granulated uniformly, and produce pellets of the similar size and composition. Our choice of binder was made taking into account results of previous studies (Mangwandi et al., 2014). The widely used carboxymethylcellulose binder was not suitable in this research as it is water soluble; the resultant granules would disintegrate when coming into contact with the waste water. It seems that polyvinyl acetate (PVAc) might give better results in the granulation of dissimilar materials and it is water insoluble.

The main aim of this research was to develop a low-cost and effective sorbent for water treatment of both anionic and cationic pollutants, as well as neutralization of acidic water. Limestone seemed to be one of the most suitable candidates for acidic water neutralization as well as for removal of a number of pollutants. Limestone is a commercial material for acidic neutralization of water and agriculture's grounds (Iakovleva et al., 2015; Mangwandi et al., 2014). This work proposes the novel approach to the treatment of waste water from cationic and anionic dyes using the same sorbent. In order to improve the adsorption properties of the limestone, a combination of limestone and coffee wastes will be used in this research. In this study, coffee waste and limestone were co-granulated using PVAc as binder. The strength and wettability of granules, as well as their reuse and resistance to liquid solutions were determined. Adsorption properties of new adsorbents were tested for their ability to remove MB and OR. The competition of removal of both cationic and basic dyes from complex liquid was examined.

2. Raw materials

Limestone was provided by Killwaughter Chemical Ltd UK. The CW was collected from the cafeteria at Queen's University Belfast, Rami cafeteria of Mikkeli and Green Chemistry Laboratory of Lappeenranta University of Technology. Before use, CW was washed with distilled water, and oven dried for 12 h at 60 °C.

Polyvinyl acetate (PVAc) and acetone by MERCK UK were used as a binder in the granulation process. Solution of PVA was prepared by dissolving a known mass of the PVA_C (from 10 to 40%) in acetone. The mixture was stirred for about 20 min at 60 °C to obtain a homogenous solution. The viscosities of the binder solutions were determined by the Haake Viscotester C.

3. Co-granules production

A small bench scale high shear granulator (KENWOOD KM070 (Japan) was used for the granulation of materials. The known mass of limestone powder and coffee waste were added to the mixer and mixed without binder for 60 s. The known value of binder was added to the powder during the next 30 s without stopping the rotator. The mixing of powder was performed at an impeller speed of 490 rpm and binding occurred within 60 s until the formation of granules.

4. Characterization of raw materials and co-granules

4.1. Spectral and physics characterization

The particle size distribution was determined using dispersion analyzer LUMiSizer 610/611 (GmbH). The measurements were performed thrice.

The chemical composition and organic elemental analysis of raw materials were determined with an energy dispersive X-ray fluorescent (ED XRF) analyzer X-Art (Joint Stosk Company Comita, St. Petersburg, Russia) and CHNS-O analyzer (Flash 2000 Elemental Analyzer, Thermo Fisher Scientific, UK), respectively.

FTIR spectra of raw materials and granules were recorded with a Bruker Vertex 70v spectrometer. Spectra were collected in the mid infrared region (4000–400 cm^{-1}) averaging 124 scans with 4 cm^{-1} resolution. Samples were prepared by the standard KBr pellet methods.

The samples were characterized with nitrogen sorption at 196 °C using TriStar 3000 (Micromeritics Inc., USA). The specific surface area of samples was calculated using the Brunauer-Emmett-Teller (BET) theory.

Microstructure of the raw and produced materials was examined using a scanning electron microscope (SEM, Nova Nano SEM 200, FEI Company). The experiment was carried out at low vacuum condition in secondary electron mode. For the analysis, samples were covered with a gold layer.

In order to study the effect of binder viscosity on the co-granulation process, different granulation experiments were carried out using binder solution of different concentrations whilst maintaining the other processing conditions constant. All experiments were carried out at room temperature (24 °C) with mixing time and speed of 2 min and 490 rpm, respectively.

The effect of the L and CW ratio on the granulation process was studied using different amounts of each material. The granules were dried for 12 h at 80 °C. The dried granules were separated according to size by sieving. The percentage of co-granules in each size range was calculated by following equation:

$$n = \left(\frac{m_i}{m_t}\right) \times 100\% \quad (1)$$

where m_t and m_i are initial and total the measure range mass of co-granules, respectively.

Granules strength was measured from diametric compression of the single granules using previously described method using Eq. (2).

$$\sigma = 2.8 \times \left(\frac{F_i}{\pi D^2}\right) \quad (2)$$

where F_i *(Newton)* is compressive force during testing of granules strength, i is number of tests, D *(mm)* is granules diameter.

Granules wettability was tested by mixing a known mass of granules with water at ambient temperature for 72 h. After testing, all granules were oven dried for 12 h at 80 °C. The strength and size of granules were determined before and after wettability tests.

4.2. Batch adsorption experiments

Sorption tests of pollutants were conducted by mixing a known weight (from 0.5 to 40 g L^{-1}) of L, CW, PVAc and LCW with 15 ml of synthetic solution of MB and OR. The concentration of dyes on the synthetic solution ranged from 5 to 20 mg L^{-1}. The experimental solutions were shaken by a shaker ST5 (IKA KS 4000i Control) from 1 to 720 h. 10 mL solutions were taken from flasks at known time