Journal of Environmental Management 206 (2018) 215–227

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Facile synthesis and characterisation of AlNs using Protein Rich Solution extracted from sewage sludge and its application for ultrasonic assisted dye adsorption: Isotherms, kinetics, mechanism and RSM design

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A R T I C L E I N F O

Article history:
Received 20 July 2017
Received in revised form
10 October 2017
Accepted 12 October 2017

Keywords:
Protein rich solution
Aluminium nanosheets
Ultrasonication
Isotherms-kinetics
Box-Behnken design
Fractional adsorption

A B S T R A C T

Protein Rich Solution (PRS) was prepared from the sewage sludge with ultrasonic assistance. With PRS, aluminium based nanosheet like materials (AlNs) were synthesised for the ultrasonic removal of Congo Red (CR) and Crystal Violet (CV) dyes. PRS was characterised by UV, EEM and NMR spectral analysis. AlNs were characterised by FTIR, XRD, TGA, BET, SEM, AFM, TEM and XPS analysis. The point of zero charge of AlNs was found to be 5.4. The BET analysis ensured that the average pore diameter and total pore volume of AlNs as 8.464 nm and 0.11417 cc/g respectively. The efficacy of AlNs for the removal of toxic dyes was tested by performing Response surface methodology (RSM) designed experiments. The effect of sonication time, dosage and initial concentration on dye removal was studied at an optimised pH value. Langmuir, Freundlich and Temkin isotherm models were examined. The maximum adsorption capacity was found to be 121.951 and 105.263 mg/g for CR and CV respectively. The kinetic models like pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion were examined to understand the mechanism behind it. The results revealed that the use of ultrasonication enhanced the mass transfer. The experimental studies on the influence of ultrasound power indicated a positive relation with the removal efficiency. The results of thermodynamic study revealed that the process was spontaneous and exothermic for both the dyes. The increase in ionic strength increased the removal efficiency for both CR and CV. RSM predicted the optimum adsorbent dosages as 0.16 g for 50 mg/L of CR and 0.12 g for 100 mg/L of CV dye solutions. The values of half-life and fractional adsorption for both CR and CV suggested that the low cost AlNs has high potential to remove the toxic industrial dyes.

1. Introduction

The rapid urbanisation and industrialisation have led to the increased use of dyes in industries for the past few decades (Bhargavi and Maheshwari, 2015). Industries like textile, leather and tanning, plastics, cosmetics, paper, etc. generate more than 700,000 metric tonnes of dyestuff with over 100,000 dyes that are commercially available today of which about 10% of the total production is discharged in textile and related industrial effluent. Especially, the textile industry effluents cause esthetical and toxicological damages to the receiving water bodies (Deng et al., 2016). Mostly, coagulation–flocculation, electrochemical, aerobic or anaerobic, membrane filtration and adsorption methods are used for the treatment of coloured wastewater. Adsorption is the most widely used method for dye removal among these processes because of its simple design, easy operation, cost efficiency, high removal capacity and as it does not produce any secondary pollution (Deng et al., 2016).

Recently, the rapid development of nanotechnology has persuaded the researchers to explore the use of different green synthesised nanoparticles for the adsorption of contaminants from wastewater for their smaller size, larger surface area, higher recovering capacity, reusability and enhanced thermal and magnetic properties (Kataria et al., 2016). Specifically, because of its higher strength, resistance to molten metal attacks, chemical inertness and electrical insulation characters, aluminium

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https://doi.org/10.1016/j.jenvman.2017.10.032
0301-4797/

nanoparticle is considered as one of the essential material in the environmental application. It has various crystal structures in which α and γ have been given more importance. Recently, more interest is shown to γ-alumina since it is stable over higher temperature and relatively high surface area. Various procedures have been carried out for the synthesis of metal oxide nanoparticles. Earlier, Fengbin Lei et al. has synthesised Al_5O_6N using plasma technique (Lei et al., 2009). Herein, a novel synthesis route was adopted for the synthesis of aluminium sheets like (AlNs) particles and its efficacy for the removal of dyes were tested. The aluminium based nanosheet like materials (AlNs) used in this study was synthesised using Protein Rich Solution (PRS) prepared from the sewage sludge.

The proteinaceous materials can be recovered from fish processing, cheese manufacturing and poultry industries, the sewage sludge, a waste which is generated across the world in large quantities, could be a vital source for the polymeric proteinaceous material. Extracellular polymeric substances (EPS), is made up of several organic materials like protein, polysaccharide, nucleic acid, amino acid and lipids etc. (Feng et al., 2013). The abundant availability of negatively charged functional groups in Extracellular Polymeric Substances (EPS) serves as ligands of heavy metals (Gao et al., 2009). Such protein-based nanoparticles have superior interests since they are biodegradable, can be easily manipulated and there are numerous possibilities for surface alteration (Weber et al., 2000). Besides, such protein functionalised AlNs is expected to overcome the difficulties of conventional adsorbents, especially higher uptake capacity. Donia et al. functionalised the magnetic silica with amine groups and reported that the adsorption capacity was increased for the adsorption of Acid Orange 10 (Atia et al., 2009). The adsorption of metals by EPS has been extensively studied earlier (Wei et al., 2015). However, the use of PRS from sewage sludge for synthesising the nanosheets and its application for the dye removal has not been carried out till now.

The advantages of ultrasonic-assisted adsorption make it a popular technique over other conventional techniques (Azad et al., 2016). Ultrasonic-assisted adsorption shows significant improvements such as the reduced adsorbent quantity, increased efficiency and reduced contact time (Asfaram et al., 2016a, 2016b). The transmission of ultrasonic shock waves through a liquid produces acoustic cavities. These shock waves create microscopic turbulence that surrounds neighbouring solid particles (Saad et al., 2017). The reactive surface of the adsorbent is activated because the mass transfer rate by convection is increased by the ultrasound irradiation. The effect of US on adsorption of various pollutants have been studied recently and reported different outcomes. For example (Li et al., 2002), have stated that the uptake of phenol was high in the absence of US than in the presence. In contrast, the study report of (Schueller and Yang, 2001) indicates a positive effect on the phenol removal using ultrasonication. As well, the increased divalent metal removal in the presence of US was reported by (Entezari and Soltani, 2008).

The main objective of this research work is (i) to prepare the PRS from domestic sewage effluent with ultrasonic assistance, (ii) to facile synthesis the AlNs using PRS, (iii) to investigate the efficacy of synthesised AlNs for the removal of Congo Red (CR) and Crystal Violet (CV) dyes using ultrasonication and (iv) to examine the effect of various influencing parameters like ultrasonication time, adsorbent dosage and initial dye concentration and to statistically optimise them.

Table 1
Characteristics of raw sludge.

Parameters	Values
pH	7.5
Electrical conductivity (ms/cm)	3.157
Total solids, TS (mg/L)	15428
Moisture content (%)	95.16
Dry solids (g)	2.118
Turbidity (NTU)	113.3

2. Materials and methods

2.1. Materials

AlNs synthesised from PRS were used for the removal of anionic and cationic dyes. The detailed procedure for the preparation of PRS and the synthesis of AlNs are presented in the later section. CR and CV were selected as target pollutant. The details of the dyes are provided in Table S1. The chemicals used in this adsorption study were of analytical grade. CR, CV, sodium hydroxide (NaOH) and aluminium nitrate $(Al(NO_3)_3)\cdot 9H_2O$ were purchased from the Nice Chemicals Pvt Ltd, India. The domestic sewage sludge sample for the preparation of PRS was collected from the wastewater treatment plant, of VIT University. The treatment plant can treat 400 m^3 of wastewater per day. The collected sludge sample was refrigerated at 4 °C for further use. The basic characteristics of raw sludge is presented in Table 1.

2.2. Methodology

2.2.1. Preparation of PRS

A combined ultrasonication – centrifugation method was used for the preparation of PRS from the sewage effluent. The sewage effluent was sonicated at 20 kHz (480 W) for 10 min using a probe sonicator (Sonics VCX 750). During the sonication, the temperature of the effluent was maintained approximately at 4 °C via ice-water bath to avoid the increase in temperature. Later, the liquor was centrifuged at 20,000 × g at 4 °C for 20 min in 50 mL tubes. The supernatant was termed as PRS and preserved in refrigerator for further use.

2.2.2. Characterisation of PRS

The Nuclear Magnetic Resonance Spectroscopy (NMR) was performed in dimethylsulfoxide (DMSO) solution to confirm the identity of the sample. The ^1H NMR spectra of PRS was obtained from Bruker Ascend™ 400 spectrometer. The modified Lowry method (Yu et al., 2007) by using the bovine serum as the standard was followed to determine the protein content of the PRS solution. Anthrone method (Yu et al., 2007) by using glucose as the standard was used to determine the polysaccharides content. The spectral information about the protein content present in PRS was determined using three-dimensional excitation-emission matrix (EEM, Hitachi Fluorescence Spectrophotometer – F 7000) and UV–Visible spectrophotometer (Spectroquant, Pharo 300). The single crystal data for dried PRS (PRS was dried at 105 °C for 5 h) was performed using XRD – Bruker, D8 Advance instrument. The functional group of dry PRS powder was studied by a Fourier Transform InfraRed Spectroscopy (FTIR, Shimadzu IR Affinity-1) (Shuibo et al., 2014).

2.2.3. Synthesis of AlNs

The nanosheets were synthesised using PRS as a template. Briefly, 1 g of $Al(NO_3)_3\cdot 9H_2O$ was dissolved in 10 mL of PRS under continuous stirring for 20 min at 60 °C. Under vigorous stirring, 0.1 N NaOH solution was added dropwise to adjust the pH of the solution to 10. Then, the suspension was centrifuged (REMI R24) at 5000 rpm for 15 min. Afterwards, the precipitate was washed with distilled water and methanol for three times and then dried in a hot air oven at 100 °C for an hr (Sutradhar et al., 2013).