Journal of Environmental Chemical Engineering 5 (2017) 1843–1854

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Silver Nanoparticle loaded corncob adsorbent for effluent treatment

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ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form 9 March 2017
Accepted 17 March 2017
Available online 18 March 2017

Keywords:
Adsorption isotherms chemical oxygen demand
Corncob
Kinetic models
Silver nanoparticle
Inactivation

ABSTRACT

In this paper, agricultural waste corncob has been modified by loading with silver nanoparticle to prepare an adsorbent for the treatment of wastewater and microbial inactivation. The silver nanoparticle loaded corncob was characterized by UV spectroscopy, FourierTransform Infrared (FTIR) analysis, Scanning Electron Microscopy with Energy Dispersive X-ray Spectrocopy (SEM-EDX), Brunauer, Emmett and Teller (BET) Surface Area analysis. The loading of 0.9 ($\pm$0.05) mg/mL and 0.92% silver nanoparticle on corncob was confirmed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Atomic Absorption Spectrometry (AAS). The treatment of wastewater onto silver nanoparticle loaded corncob has been studied for Chemical Oxygen Demand (COD) reduction and showed a significant COD reduction of 77%, 89% and 97% for tannery, dairy and canteen effluent visa versa. The adsorption isotherm was fitted well by the Langmuir and the adsorption kinetics was well described by Pseudo-first order. The silver nanoparticle loaded corncob was potential against *E. coli* inactivation and the inactivation kinetics were well described by Homs model. The spent adsorbent was regenerated and used upto 3 cycles and found that the non detectable range of *E. coli* upto 3 cycle.

1. Introduction

Discharge of untreated wastewater to the environment causing adverse effects to the human beings and alter the ecosystem. The microbial contamination of wastewater causes various diseases to the people whom explored on it. In particularly the wastewater from the industrial sector, tannery effluent contains high Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), suspended solids, sulfide, heavy metals and microbial contaminants [1]. The wastewater from domestic sector, dairy and canteen effluent contains fats, nutrients, detergents, sanitizing agents and microbial contaminants [2]. Discharging these effluents into the environment, particularly natural water bodies that causes eutrophication, algal boom and health threat to people. The wastewater treatment that includes the biological treatment such as activated sludge process, lagoons, sequential batch reactor, anaerobic sludge blanket, etc., have the disadvantages such as requirement of larger area, large reactor and high energy input etc.

Various advanced techniques have been used for wastewater treatment such as membrane process [2] ultraviolet exposure, oxidation processes using TiO_2/UV, H_2O_2/UV, photo fenton, ozonization process [3], photocatalytic and photoelectrocatalytic methods have the shortcomings of high investment, maintenance costs, tedious procedure and emission of secondary pollution in the form of sludge. Among the treatment methods adsorption has been reported to be an advantageous method [4]. In recent years nano-particles prove to have great advantage over the existing methodologies in wastewater treatment processes and nano-particles possess a unique structure and highly reactive properties, which makes them as powerful absorbents.

Nanoparticles can be functionalized with various chemical groups to increase their adsorption properties [5]. Previous studies were reported that the increased adsorption efficiency was achieved by fabricating the nanoparticles with the absorbent surface for water treatment processes. Many investigations have been reported that nanoparticles loaded adsorbents for wastewater treatment such as silica loaded with silver nanoparticles [6], chitosan loaded with silver nanoparticle [7], silver nanoparticles incorporated clay [8] and activated carbon loaded with silver nanoparticles [9]. In order to prepare a low cost adsorbents, agricultural waste materials have been considered. The agro-wastes such as rice husk [10], coconut husk [11], peanut wastes, sugarcane bagasse, corncob [12] etc., have been reported as a low cost adsorbent. Among the agro-industrial wastes, corncob was not much explore have been taken for the present study. The corncob had been reported for 79% of dye removal [12] and 80% of COD reduction [13]. Previous studies reported that the activation of

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http://dx.doi.org/10.1016/j.jece.2017.03.020
2213-3437/

Nomenclature

C_e	Equilibrium concentration (mg/L)
C_0	Initial concentration (mg/L)
q_e	Equilibrium concentration (mg/g)
q_0	Maximum adsorption capacity (mg/g)
b	Langmuir binding constant.
R_L	Dimensionless separation factor
K_F	Freundlich constant $((mg/g)(L/mg)^{1/n})$
n	Heterogeneity factor
K_R	Redlich–Peterson constants(L/mg)
α_R	Redlich–Peterson constants $(mg/L)^{\beta}$
β	Redlich–Peterson isotherm exponent
K_S	Sips isotherm constant $(mg/L)^{(1/n)}$
q_m	Monolayer capacity (mg/g)
(1/n)	Sips isotherm exponent
K	Rate constant $(mgL^{-1} min^{-1})$
C_i	Initial concentration of pollutant (mg/L)
C_t	Concentration of pollutant (mg/L) at time t
K_1	Rate constant of first order (min^{-1})
K_2	Rate constant of second order $(L\,mg^{-1}\,min^{-1})$
K_3	Rate constant of third order $(mg^2\,L^{-2}\,min)$
q_e	Final COD concentration at equilibrium (mg/g)
q_t	Final COD concentration at time t (min)
K_{1p}	Pseudo-first order kinetic constant (min^{-1})
K_{2p}	Pseudo-second order kinetic constant $(g\,mg^{-1}\,min^{-1})$
α	Initial adsorption rate constant $(mg\,g^{-1}\,min^{-1})$
β	Monolayer coverage of the adsorbent $(g\,mg^{-1})$

corncob by KOH/K_2CO_3 and CO_2 for obtaining large surface area [14] and the improved mechanical strength by alkali (NaOH) treatment [15]. The better adsorption efficiency of 91% using milled corncob was reported on dye removal by Robinson et al. [16]. Cellulose fibers with Ag-loading SiO_2-nano antibacterial material has potential against *E. coli* and *Staphylococcus aureus* [17]. According to these literature studies, further improvement of milled corncob powder activation by alkali treatment was adopted for better adsorption. The ecofriendly cost effective, biological synthesis of silver nanoparticle using *Pseudomonas putida* NCIM 2560 was used as an antibacterial agent. The novel adsorbent preparation was attempted from the waste material loaded with a bactericidal silver nanoparticle. The agricultural waste corncob was used as an adsorbent, improvised by loading with silver nanoparticle. The prepared adsorbent was regenerated at low cost and no sludge formation. The ease of management and reusability of the prepared adsorbent was suitable for industrial wastewater treatment.

The high levels of pollutants in the form of COD, TDS, TSS and microbial contamination in water are unsuitable for irrigation or any other uses. Among the treatment technologies, adsorption process was suitable for treating industrial wastewater. However, most of the adsorbents prepared were reported for its effective removal of metal ions, dyes at lower concentrations of synthetic effluent prepared in the laboratory and the complementary effects in the real effluent was not explored. Hence the present study has been reported the preparation of silver nanoparticles loaded corncob adsorbent. The applicability of the prepared adsorbent was investigated by treating the real effluent samples from tanneries, dairy and canteen effluent using silver nanoparticle loaded corncob adsorbent for COD (Chemical Oxygen Demand) reduction and inhibition of *E. coli* growth.

2. Materials and methods

2.1. Materials

Analytical grade sodium hydroxide, aniline, hydrochloric acid, potassium persulfate were procured from Sigma-Aldrich chemical, India. Corncob was obtained from the local market in Chennai, India. The untreated tannery, dairy and canteen effluents were collected from the Avadi Tannery plant, Sholinganallur Aavin dairy plant and Anna University Canteen, Chennai, India.

2.2. Preparation of activated corncob

Raw corncob was broken into pieces (~3 cm); and the soft pith portions were removed, and the hard woody portions were washed with boiling water, and dried in an oven at 80 °C for 3 h [18]. The dried corncob pieces were pulverized and sieved to 1.5 mm size. Corncob powder (50 g) was activated by alkali in 5: 1 ratio (10 g NaOH) and refluxed at 160 °C for 8 h then filtered, washed with distilled water until the solution attained a pH of 7. The oven dried (80 °C for 12 h) adsorbent was stored in an airtight container.

2.3. Preparation of silver nanoparticle loaded corncob adsorbent

The cost effective and ecofriendly synthesis of silver nanoparticle using bacterial strain *P. putida* NCIM 2560 was carried out. For the synthesis of silver nanoparticle, the growth (Luria-Bertani) medium was prepared by supplementing 1 mM silver nitrate and sterilized (121 °C at 15 psi). The 24 h culture of *P. putida* was inoculated in the sterilized growth medium and incubated in a rotary shaker (150 rpm) at 37 °C. The silver nanoparticle was obtained from the culture supernatant after 48 h of incubation by centrifugation (10,000 rpm, 10 min). The synthesized silver nanoparticle was extracted by a Cloud Point Extraction method using Triton X-100. 10 mL supernatant of crude silver nanoparticle was centrifuged with 1% nonionic surfactant triton X-100 of 5 mL and 0.1 mL of 3.5 mM $NaNO_3$. The centrifuged sample was adjusted to the pH of 3 with HCl solution and kept in a water bath at 65° C, cloud point temperature of Triton X-100 for 30 min. After the inference of cloudy appearance the sample was centrifuged at 10,000 rpm, for 10 min. The upper aqueous phase was drained and the lower phase rich in silver nanoparticle was washed with water and 0.1 M HNO_3 in methanol. The silver nanoparticles was dried in an oven at 100° C for over night and stored for further study.

The activated corncob powder (5 g) was functionalized with 100 mL of aniline (0.2 M aniline in 1 M HCl) followed by the addition of 100 mL of silver nanoparticle solution with varying concentration of 0.310, 0.320, 0.330 and 0.340 mg/L. The reaction mixture was continuously stirred and kept in an ice bath for 12 h, followed by the drop wise addition of 0.1 M potassium persulfate. The reaction mixture was continuously stirred for 2 h and the resultant adsorbent was filtered and washed with deionized water.

2.4. Characterization of silver nanoparticles loaded corncob adsorbent

The UV–vis spectroscopy (T 90+ UV/Vis SPEC PG Instruments Ltd.) was used for characterizing the silver nanoparticle, corncob powder, and silver nanoparticle loaded corncob in an automated wavelength range of 200 to 600 mm. UV-spectrum measurements were taken at room temperature, using 1 cm pathlength cuvette.

The functional groups present in the adsorbent were analyzed by Fourier Transform Infrared Spectroscopy (FTIR – Perkin Elmer Spectrum 400) in a wavelength range of 4000 to 400 cm^{-1} and at a resolution of 4 cm^{-1}, to evaluate the authentification of the silver nanoparticle and corncob by their functional groups. Potassium