International Journal of Biological Macromolecules 112 (2018) 294–305

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: https://www.journals.elsevier.com/ijbiomac

Effective adsorption of oil droplets from oil-in-water emulsion using metal ions encapsulated biopolymers: Role of metal ions and their mechanism in oil removal

S.SD. Elanchezhiyan [a], Subbaiah Muthu Prabhu [a,b], Sankaran Meenakshi [a,*]

[a] Department of Chemistry, The Gandhigram Rural Institute-Deemed to be University, Gandhigram 624 302, Tamil Nadu, India
[b] Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:
Received 13 November 2017
Received in revised form 26 December 2017
Accepted 17 January 2018
Available online 31 January 2018

Keywords:
Oil adsorption
Emulsion
Metal ions
Biopolymers
Intercalation

ABSTRACT

Herein, synthesized and compared the three different kinds of hybrid bio-polymeric composites viz., lanthanum embedded chitosan/gelatin (La@CS-GEL), zirconium embedded chitosan/gelatin (Zr@CS-GEL) and cerium embedded chitosan/gelatin (Ce@CS-GEL) in terms of their oil uptake efficiency. The adsorption efficiency was studied under various optimized parameters like contact time, pH, dose, initial oil concentration and temperature. The oil adsorption capacity was found to be 91, 82 and 45% for La@CS-GEL, Zr@CS-GEL and Ce@CS-GEL composites respectively. The metals were used as a bridging material to connect both CS and GEL using the hydrophilic groups to enhance the oil recovery by hydrophobic interaction. Also, the introduction of metal ions on the surface of biopolymers would modify the oil/water properties which in turn, decrease the interfacial tension between oil and water phases. The mechanism of oil uptake was explained using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscope (SEM), energy dispersive X-ray (EDAX) and heat of combustion. The experimental data confirmed Langmuir isotherm as the best fit for oil adsorption process. Thermodynamic parameters such as standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) indicated that the oil adsorption was spontaneous and endothermic. The oil adsorption mechanism was established based on isotherm and thermodynamic models.

1. Introduction

In the past few decades, the challenging complication of copious pollutants has been identified in the aquatic region throughout the world because of increasing demands of human requirements and revolution in engineering products. Among them, organic contaminants like emulsified oil in water bodies has introduced permanent harmful effects to the environment and is known to be carcinogenic in nature which has been confirmed by the international agencies for research on cancer [1–6]. For this reason, most of the researchers have been motivated towards extensive research on oil recovery from oily wastewaters. A large amount of oily wastewater is commonly generated during different kinds of manufacturing processes like food production, textile, paper, petrochemicals, metal processing industries, etc. [7,8]. In addition, the presence of oil in industrial effluents can be found in a wide range of concentrations in various forms like fats, lubricants, chemical additives, light and heavy hydrocarbons, heteroatom, etc., [9,10] and usually dispersed as oil-in-water emulsion which contains aliphatic and aromatic components that can't be degraded easily. The threat of oil pollution has become a worldwide concern owing to hazardous components present in oily wastewater in the form of oil-in-water emulsion and even very low oil concentration would pave the way towards severe ecological problem to the living organisms. Thus, focus should be made to address the retrieval of oil molecules from wastewater before disposing them.

Even though there are many conventional methods such as flocculation [11], coagulation [12], adsorption [13,14], membrane techniquees [14], etc., exploited towards the recovery of oil from oily wastewater, adsorption is traditionally used and exhibited greater efficiency. Besides, it's a simple process, eco-friendly, low-operational expenditure and easy recovery of adsorbent. Owing to these reasons, the adsorption technique is received much attention. Thus, many environmental scientists have focusing their research to identifying the novel adsorbents for oily wastewater. The adsorbents such as activated carbon [15], biopolymers [16], nanoclay [17], sawdust [18], vermiculite [19], walnut shell [20] etc., have been recorded as outstanding, in the literature due to their higher efficiency towards the removal of oil molecules. However, preference would be given to biopolymers due to its biocompatibility, biodegradability, high adsorption property, eco-friendliness, low cost, etc., and typically used in bioremediation (wastewater treatment) owing to active multifunctional groups and it can be easily modified

* Corresponding author.
E-mail address: sankaranmeenakshi2014@gmail.com (S. Meenakshi).

https://doi.org/10.1016/j.ijbiomac.2018.01.118
0141-8130/

according to requirements [21]. In recent days, a significant number of materials have been developed as adsorbent for the immobilization of oil droplets, but it is the need of urgent to identify the adsorbents possessing higher adsorption capacity, low cost and abundance. Chitosan is a well-established biopolymer contains a high content of amine and hydroxyl groups which play a vital role in the chemical modification [21]. Similarly, gelatin also considered as a well-known biopolymer obtained from collagen and having amino group and carbonyl group in the polypeptide chain, many carboxyl group in the side chain of polymeric matrix [22]. The unmodified form of base materials (i.e., chitosan, gelatin, etc.) were not effective towards the removal of water contaminants. Thus, researchers have paid much attention to investigate a new class of adsorbent. In recent years, hybrid adsorbents have received much attention among various adsorbents owing to high adsorption efficiency, high surface area and strong affinity towards the target pollutants and due to these reasons hybrid adsorbents become environmentally sound in wastewater treatment [23]. Usually, hybrid adsorbents show better adsorption capacity than any of its constituents used alone. The significant number of hybrid adsorbents have been synthesized and successfully utilized for the removal of different kinds of toxic ions such as fluoride [24], arsenic [25], uranium [26], chromium [27], etc. Both biopolymers facilitate cross linking with multivalent metal ions due to the amino groups present in the polymeric matrix. Multivalent metal ions embedded biopolymers have been projected as potential adsorbents in the wastewater treatment owing to their strong affinity towards targeted pollutants. However, transition metals have better chelating ability with functional groups present in the biopolymers and possess the higher adsorption capacity because of their strong affinity, less leaching effect, binding tendency and higher positive charge [28].

Hence, chitosan and gelatin have been studied with appropriate modification of metal ions viz., La^{3+}, Zr^{4+} and Ce^{3+} was synthesized and evaluated the oil removal efficiencies via different metal ions embedded biopolymeric composites like La@CS-GEL, Zr@CS-GEL and Ce@CS-GEL. The effect of physico-chemical parameters viz., pH, contact time, adsorbent dosage and initial oil concentration on oil removal efficiency was investigated. The prepared adsorbents show better adsorption capacities compared to their parent polymers. The virgin and the oil sorbed adsorbents were characterized using SEM, EDAX, FTIR, XRD, TGA and heat of combustion. Adsorption isotherms and thermodynamic parameters were employed to investigate the mechanism of oil recovery from oil-in-water emulsion. Metal ions embedded binary biopolymeric composites have not been reported to date for the retrieval of oil molecules from oily wastewater.

2. Experimental section

2.1. Materials

Chitosan (85% deacetylated) was supplied by Pelican Biotech and Chemicals Labs, Kerala (India) and the material was directly used without any further purification. Gelatin was supplied by Merck, (Germany). Commercial cutting oil was obtained from local market, Tamil Nadu, India and the following analytical grade chemicals like n-Hexane (Merck, Mumbai), lanthanum chloride heptahydrate (98%), zirconium oxychloride octahydrate (99.9%), cerium chloride heptahydrate (99.9%) (Sigma Aldrich, Mumbai) Glutaraldehyde, hydrochloric acid and sodium hydroxide (Merck, Mumbai) were used in this study. All the experimental solutions were prepared using double distilled water and used throughout the study.

2.2. Preparation of oil-in-water emulsion

A synthetic oil-in-water emulsion was prepared by adding 4 g of commercial cutting oil in 100 mL deionized water with gradual stirring. Using magnetic stirrer (200 rpm), the resulting milky solution was stirred for 1 h and treated as oily wastewater. The oily wastewater was composed of aliphatic and aromatic hydrocarbons. Appropriate amount of oily wastewater was used to prepare different oil concentrations and the properties of cutting oil are given in Table 1. The zeta potential and particle size values provide a clear conception regarding the formation of stable oily wastewater.

2.3. Synthesis of metal ions embedded chitosan/gelatin biopolymeric hybrid composites

Metal ions embedded chitosan/gelatin biopolymeric hybrid composites viz., La@CS-GEL, Zr@CS-GEL and Ce@CS-GEL were synthesized as follows: About 2 g of raw chitosan (85% deacetylated) was dissolved in (2% v/v) aqueous solution of acetic acid and stirred for 1 h to get a homogeneous chitosan solution. Then, 2 g of gelatin was weighed and dissolved in 5% metal solution and stirred for 30 min to get homogeneous solution. The dissolved mixtures were stirred for 6 h and 5% of glutaraldehyde solution was added slowly with constant stirring for cross-linking. At 4 °C, the wet mixture was refrigerated for 24 h to undergo complete cross-linking reaction. The resulting metal ions embedded chitosan/gelatin colloidal solution was washed to remove unreacted excess ions and dried at 70 °C in an oven. The dried biopolymeric hybrid composites were ground well and sieved (60 μm) to get uniform size. Finally, the resulting material was stored for oil adsorption studies and the method of preparation is illustrated in Scheme 1.

2.4. Instrumentation

The surface morphology of the synthesized hybrid composites and oil sorbed materials were investigated using SEM analysis with VEGA3 TESCAN model and the elements present in the adsorbents were recorded in EDAX spectroscopy with Bruker Nano Gmbh, Germany during SEM observations. The FTIR absorption spectra were studied within the infrared region of 400–4000 cm^{-1} using JASCO-460 plus model, Japan. The XRD measurements were calculated using X'per PRO model-PANalytical, Netherland. TGA was carried out using Model 2960, Universal V2.4F TA instruments (The United States). Heat of combustion values of the adsorbents were studied using Model Parr 6200 Calorimeter (Parr Instruments Company, The United States). The pH measurements were carried out using expandable ion analyzer EA940 with the pH electrode (The United States). The pH at zero point charge of prepared adsorbents was measured using the pH drift method.

2.5. Adsorption experiments

Oil adsorption experiments were carried out by batch equilibrium method in triplicate. A known volume of oily wastewater containing 4% of initial oil concentration was treated with a fixed amount of adsorbent at acidic pH in room temperature. Using a mechanical shaker, the mixture was shaken thoroughly at a speed of 180 rpm to attain equilibrium and the filtrate was analyzed for residual oil concentration at the appropriate time. The adsorption experiments were repeated for each

Table 1
Properties of cutting oil selected for this present study.

S. no.	Characteristics	Method	Specification
1	Appearance @ 30 °C	Visual	Clear liquid
2	Density @ 29.5 °C, g mL^{-1}	IS 1115-86 P: 32	0.869
3	Water content, % wt.	IS 1115-86 P: 40	1.6
4	Flash point, (COC), °C	IS 1115-86 P: 69	176
5	Kinematic viscosity @ 40 °C, cSt.	IS 1115-86 P: 25	24.1
6	Particle size of 4% cutting oil emulsion, mμ	CILAS 930 particle size analyzer	1.66
7	Zeta potential value, mV	Malvern zeta seizer	−90.9
8	Sulfur compounds (%)	GC mass	5