INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–7

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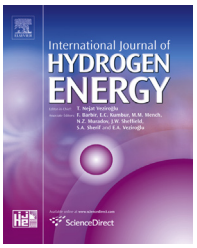

Sustainable harvesting of aqueous phase fatty acids by expanded graphite and isopropyl alcohol

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ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form
15 July 2016
Accepted 19 July 2016
Available online xxx

Keywords:
Fatty acids
Harvesting
Expanded graphite
Adsorption
Extraction
Regeneration

ABSTRACT

Fatty acids (FA) from organic wastes are environmentally friendly raw materials with high economic value ranging from fuels to oleo-chemicals for growing diversity of products. In this study, expanded graphite (EG) and isopropyl alcohol have been used to adsorb and concentrate the low content of FA in aqueous solution to replace the existing solid-phase extraction methods. The results showed that the maximum adsorption capacity of EG was more than 8.2 g-FA/g due to the inter-latticed structure of graphene sheets, and subsequent coalescence of FA droplets. The extraction efficiency of isopropyl alcohol was always higher than those of dichloromethane and ethanol for the recovery of absorbed FA due to the lower surface tension and higher miscibility with water. After 5 times of recycle, although the specific FA adsorption was decreased 42% of raw EG, extraction efficiencies by isopropyl alcohol were not changed. In conclusion, our study suggested that the EG and isopropyl alcohol could achieve the efficient and environmentally friendly harvesting of low concentration of FA in aqueous solutions during the biological conversion of organic matters in food waste.

Introduction

Anaerobic digestion converts organic matters from biomass into biogas (mixture of mainly H_2, CH_4, CO_2), organic acids, alcohols, etc. [1]. Among these products, fatty acids (FA) are raw materials for growing diversity of products ranging from fuels to oleo-chemicals due to its energy-rich, environmentally friendly, and economic value properties. Most of FAs were extracted from either plant or animal sources using traditional analytical methods, which the procedure usually required a relatively long-time and conventional solvents such as hexane, chloroform, methanol [2–4].

Recently, some microorganisms such as algae and cyanobacteria have gained a lot of attention owing to their capability of producing and accumulating FAs inside their body. For example, purple non-sulphur (PNS) bacteria, which have been

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http://dx.doi.org/10.1016/j.ijhydene.2016.07.153

the most intensively studied photosynthetic H_2-producing bacteria due to their demonstrated high substrate conversion yields, are reported to synthesize fatty acids during H_2 fermentation [5]. Although PNS could be simply cultivated than other FA producing microorganisms such as algae, the oil content of PNS bacteria ranged 20–40% of dry biomass weight, which is too low to gain economic feasibility [6].

Microalgae appear to be a more promising feedstock option for FA production [7]. They have several advantages over traditional oilseed crops and their simplicity single-cell structure allows for a potentially high lipid productivity, which contains significant amount of polyunsaturated fatty acids and other compounds such as vitamins, proteins, pigments, etc., which are of considerable value to the nutraceutical, pharmaceutical, cosmetic, and human and animal food industries [7–11]. Under unfavorable culture conditions, microalgae are able to store neutral lipids from 20% to 70% of their mass in heterotrophic or autotrophic ways, mainly in the form of triacylglycerol [12]. During the cultivation of bacteria such as *Rhodopseudomonas palustris* under anaerobic light condition, lipid content ranged from 22% to 39% of dry biomass was observed [6,13]. It has been reported that bacteria can also accumulate fatty acids up to the oil content of 40% of their dry-biomass [14]. As a novel solution, the genetically engineered cyanobacteria and *Escherichia coli* have proven to synthesize FA and secrete them outside the cell, depending on the regulation of metabolism, these species produce FAs in the range of 0.1–7.0 g-FA/L [15–17].

After the bio-conversion and secretion of FA, the harvesting procedures of FAs from microorganisms including the separation, dewatering, disorganization, and FAs extraction by solvent should be followed. Solid-phase extraction (SPE) is considered as one of the most powerful techniques currently available for rapid and selective harvesting of FA. The use of activated carbon and silica columns for the separation of FA has been reported [18,19], however, requires intensive energy and environmental burden and have been accounted up to 70–80% of total cost of FA production [19,20]. Among the potential alternatives of current adsorbent for FA recovery, expanded graphite (EG) is a well-known carbon material that can be easily produced from the intercalated graphite by the heat shock at 800 °C for 1 min [21]. The intercalated graphite can be produced by chemical, electrochemical, and thermal methods with the increase of the distances between the graphite layers. As a new carbon material, EG has been used in many fields including oil adsorption [22]. The adsorption capacity of EG for oil-containing wastewaters including crude oil, engine oil, and gasoline has been reported to be high, ranging from several grams to more than 80 g/g-EG under various experiment conditions [23–26]. Moreover, it also has strong absorption to non-polar organic macromolecules no matter they are in the state of suspension, emulsification or solution. Recently, our study showed that EG could be applied for the concentration of FA from the food processing wastewater up to 8.01 g/g-EG by coalescence of FA inside the macropores [21].

After the concentration step by adsorption of FA, solvent extraction step is followed. However, the extraction of FA with chloroform, hexane, or dichloromethane involved concerns on environmental and health issues due to their high volatility with potential carcinogenicity [27,28]. Therefore, the selection of environmentally friendly solvents should consider not only the extraction efficiency but also environmental and health aspects. Alcohols have long been attractive solvents to hexane for oil extraction [29], and with respect to the use of alcohols, isopropyl alcohol and ethyl alcohol are the most promising solvents for the oil extraction [30,31].

In this study, we have addressed above issues by applying a novel approach including the application of a novel adsorbent (i.e., expanded graphite) coupled with sustainable extraction method (i.e., extraction by alcohols) for the FA recovery from aqueous solution.

Materials and methods

Materials preparation

For the preparation of expanded graphite (EG) as a novel adsorbent, acid-treated graphite fragments (EXP-527, Hyundai Coma Co., Korea) were exposed to the shock-heating at temperatures of 1073 ± 10 K in the furnace (DMF-5T, Lab House Instrument Co., Korea) for 1 min. Commercially available granular activated carbon (GAC 1240, Norit Americas Inc., USA) was used as the conventional adsorbent in order to compare with EG in adsorption of FA. Isopropyl alcohol (C_3H_8O, 99.5%, MW = 60.01 g/mol), ethyl alcohol (C_2H_6O, 99.5%, MW = 46.07 g/mol) were supplied by Sigma–Aldrich. γ-linolenic acid ($C_{18}H_{30}O_2$, MW = 278.43 g/mol, Yuhan Chemical Inc., Korea) was used as the model fatty acid aqueous solution, and was freshly prepared with deionized water before each experiment.

The surface morphology of EG were observed using a scanning electron microscope (SEM-LEO SUPRA 55, Carl Zeiss Co., Germany), field emission scanning electron microscopy (FE-SEM, Leo supra 55, Carl Zeiss Co., Germany), and the elemental composition was characterized by the energy-dispersive X-ray (EDX) at the randomly selected surface. The specific surface area and mean pore size was measured with the Brunauer–Emmett–Teller (BET) method by Quantachrome BET analyzer (USA), the determination of the surface and mean pore size were based on isotherms of adsorption and desorption of nitrogen at 77 ± 0.5 K.

Adsorption of fatty acid

Batch adsorption experiments were performed by applying 30 and 300 mg of EG and GAC, respectively, to each series glass bottles containing 200 mL of FA aqueous solution range from 100 mg/L to 2000 mg/L at 295 K. These bottles were sealed and placed in a precise shaking incubator (WIS-20, DAIHAN Scientific, Korea) at a uniform agitation speed of 150 rpm for 20 h to provide the sufficient period of time to ensure that equilibrium had been reached. FA concentration was determined by UV spectrophotometer (Shimadzu, Japan) at an absorbance wavelength of 254 nm. All of the experiments were performed in duplicate and the average values were used in the calculations.

The amount of adsorbed FA onto unit mass of EG or GAC (q, mg-FA/g) was calculated by subtracting the equilibrium

Please cite this article in press as: Do QC, et al., Sustainable harvesting of aqueous phase fatty acids by expanded graphite and isopropyl alcohol, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.153