Colloid and Interface Science Communications 18 (2017) 1–4

Contents lists available at ScienceDirect

Colloid and Interface Science Communications

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

Gas-shell-encapsulation of Activated Carbon to Reduce Fouling and Increase the Efficacy of Volatile Organic Compound Removal☆,☆☆

Albert T. Poortinga[a,*], Cees J.M. van Rijn[b]

[a] Polymer Technology, Eindhoven University of Technology, De Rondom 70, 5612, AP, Eindhoven, The Netherlands
[b] Laboratory of Organic Chemistry, Wageningen University, Stippeneng 4, 6708, WE, Wageningen, The Netherlands

ARTICLE INFO

Keywords:
Activated carbon
Encapsulation
Adsorption
Anti-fouling
Microbubbles
Aerogel
Water treatment

ABSTRACT

A method to encapsulate activated carbon particles is presented that reduces fouling of these particles with Natural Organic Matter (NOM) to preserve their adsorption capacity for Volatile Organic Compounds (VOCs) from water in the presence of NOM. The encapsulation method uses an oil-in-water emulsion template to encapsulate the activated carbon particles within a gas-filled porous shell of hydrophobic silica particles. This new 'gas-shell-encapsulation' method has little influence on the adsorption capacity of the activated carbon for a representative VOC (toluene). The adsorption of NOM components (humic acid) onto the encapsulated activated carbon is however strongly reduced such that preloading of the encapsulated activated carbon with humic acid hardly reduces its adsorption capacity for toluene, whereas for unencapsulated activated carbon preloading with humic acid reduces the adsorption capacity by roughly a factor of three.

The removal of volatile organic compounds (VOC) from water using adsorbents such as activated carbon is a method frequently applied in the cleaning of waste and surface water and in the production of drinking water. This method suffers however from fouling of the adsorbents with natural organic matter (NOM) present in the water, which can strongly reduce the adsorption capacity of the adsorbent as well as the rate of VOC removal [1–8]. Moreover, regeneration of activated carbon fouled with NOM requires pyrolysis and carbonization of the NOM followed by gasification, which are high temperature processes that decrease the lifetime of the activated carbon [9]. Several authors have studied activated carbons with different properties, such as particle size, pore size and surface chemistry, in order to reduce the susceptibility of activated carbon to NOM fouling [1–4]. In this report we encapsulate activated carbon particles within a shell of gas and study the adsorption of NOM and a VOC (toluene) on these encapsulated particles. We hypothesize that by encapsulating the activated carbon particles in gas NOM is unable to adsorb while VOCs, because of their volatility, can still reach the pores of the activated carbon. Others have studied the adsorption of VOCs from water on hydrophobic aerogels, on activated carbon of which the pores were filled with hydrophobic aerogel or on activated carbon made water-repellent by adsorbing fluorocarbon molecules to its surface [10–12]. As for the gas-shell-encapsulated activated carbon described here, also in these cases the interior of the adsorbents is expected to remain dry and VOCs first have to evaporate from the water to adsorb [10]. While the adsorption principle is thus the same, we choose to use unmodified activated carbon because the use of activated carbon constitutes a proven technology that often outperforms possible alternatives such as aerogels, e.g. in capacity at relevant adsorbate concentration and in cost price [13,14]. Furthermore, the applied gas-shell-encapsulation technique produces particles that can easily be dispersed in water even when the particles are fine, e.g. less than 100 μm. This is an advantage because for larger particles, such as the hydrophobic aerogels used by Wang et al. [14], heat and mass transfer limitations may slow down VOC adsorption [14,15]. To our knowledge, the effect of using adsorbents of which the interior remains dry on the influence of fouling by NOM on VOC removal has not been studied before.

The gas-shell-encapsulation method is an extension of the method previously used to produce gas-shell-encapsulated droplets, also referred to as antibubbles or inverse bubbles [16,17]. Gas-shell-encapsulated activated carbon particles were made as follows. Hydrophobized fumed silica particles (HDK H18 supplied by Wacker) were dispersed at 7.5% (all percentages in weight percent) in hexane using an ultrasound probe and subsequently 10% powdered activated carbon particles (supplied by Cabot) was mixed in. Hydrophobized fumed silica particles (HDK H30 supplied by Wacker) were dispersed at 0.5% in a 25%

Abbreviations: NOM, natural organic matter; VOC, volatile organic compounds

☆ Notes: The authors hold a patent on the gas-shell-encapsulation technique described in this publication.

☆☆ Author Contributions: The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

* Corresponding author.
E-mail address: A.T.Poortinga@tue.nl (A.T. Poortinga).

http://dx.doi.org/10.1016/j.colcom.2017.04.001
Received 21 November 2016; Received in revised form 14 April 2017; Accepted 17 April 2017

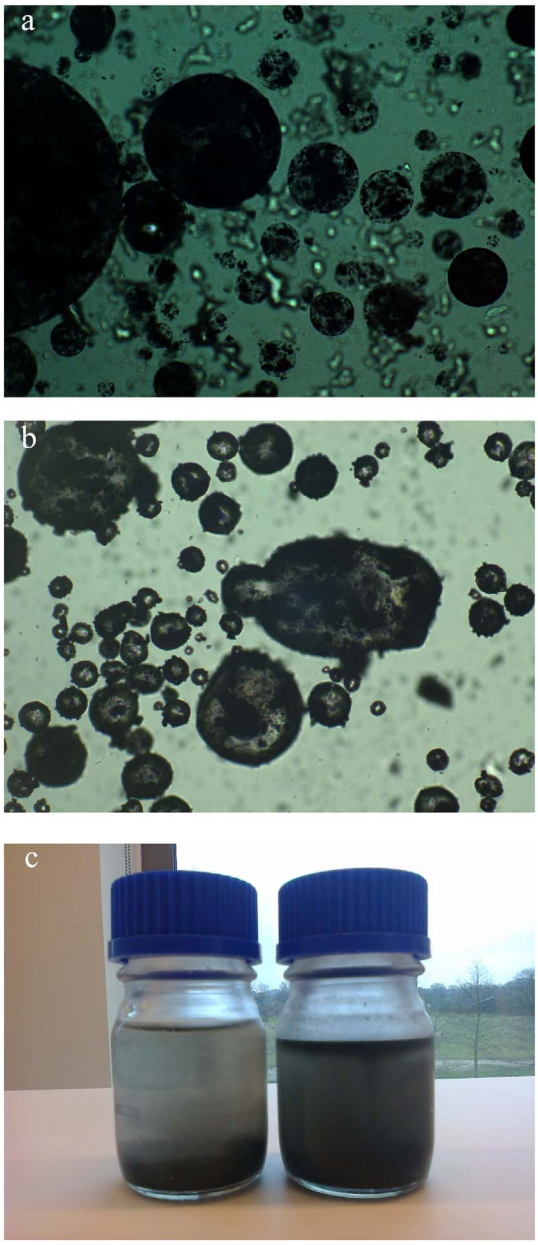

Fig. 1. (a) activated carbon particles in oil in water dispersion, (b) activated carbon particles in air in water dispersion, (c) dispersion in water of unencapsulated (left) and gas-shell-encapsulated (right) activated carbon particles when left to stand for 10 min. The width of (a) and (b) corresponds with 500 μm.

maltodextrin 15DE solution (supplied by Roquette) using an ultrasound probe. The hexane phase was dispersed at 20% in the aqueous phase using a turrax mixer (IKA werke) at 1500 rpm. The resulting particle-in-oil-in-water dispersion is shown in Fig. 1a. This dispersion was quickly frozen by contacting a 150 ml glass beaker containing 10 g of dispersion with liquid nitrogen such that a thin film of frozen dispersion is formed. This frozen dispersion was subsequently freeze-dried for 20 h using a Virtis freezemobile 25XL freeze-dryer. Freeze-drying leads to the removal of both the water and the hexane from the dispersion leading to a powder that contains 8% activated carbon. Dissolving this powder in water leads to the structures shown in Fig. 1b. A comparison of Fig. 1a and b shows that the dispersion after freeze-drying and reconstitution looks very similar to the starting dispersion in terms of structure and particle size distribution. However, in the final dispersion the structures containing the activated carbon particles show a much stronger optical contrast with the surrounding aqueous phase than in the starting dispersion. In the final dispersion these structures are also less spherical. Both observations are a sign that in the final dispersion the oil phase has been replaced with gas. Because of the low refractive index of gas more light scattering takes place at the interface giving it more contrast. Also, as a result of the relatively large solubility of gas in water the gas shell partially dissolves until stresses that develop in the shell of adsorbed hydrophobic particles that surrounds the gas shell stop the dissolution process. The resulting slightly buckled appearance of the gas shell is typical for particle-stabilized, also referred to as Pickering stabilized, bubbles [18]. The fact that in the final dispersion the activated carbon particles are entrapped within a shell of gas is also expressed by the creaming of encapsulated activated carbon particles (Fig. 1c). We hypothesize that the formation of gas-shell-encapsulated activated carbon particles proceeds as follows. During freeze-drying the volatile oil droplets containing the activated carbon particles are surrounded by a glassy matrix consisting of the frozen maltodextrin solution that becomes porous upon sublimation of the water, which allows the hexane to evaporate. This does not lead to collapse of the structure because of the mechanical strength of the glassy maltodextrin matrix. The evaporation of the oil leaves behind spherical cavities that are filled with the activated carbon particles. The activated carbon particles are surrounded by the hydrophobic particles (H18) that were dispersed in the oil phase and the spherical cavities are surrounding by the hydrophobic particles (H30) that were dispersed in the aqueous phase. During and after reconstitution the hydrophobic particles prevent the spherical cavities from being filled with water, i.e. microbubbles are formed in which the activated carbon particles are entrapped. Previously, we have shown that a similar process takes place when the volatile oil droplets contain droplets of an aqueous solution instead of activated carbon particles [16,17]. In this process, the use of H30 particles in the aqueous phase, which are less hydrophobic than the H18 particles used in the oil phase, assures that the gas-shell-encapsulated activated carbon particles can still be dispersed in water relatively easy. It should be noted that the encapsulation efficiency of the activated carbon will be somewhat below 100%. This can be seen in Fig. 1b. The small black spots in the background of this figure are small activated carbon particles that are out of focus because they are lying at the object glass plate below the microbubbles. Also, it appears that part of the smaller activated carbon particles ended up at the surface of the microbubbles, as judged by the small black protrusions present at the surface of some of the microbubbles. This is in line with flotation experiments that have previously shown that activated carbon particles have a tendency to adsorb at bubble surfaces [19].

Two types of adsorption experiments were done, both at room temperature. First, the adsorption of toluene (being a representative example of a VOC) on encapsulated and unencapsulated activated carbon was measured as a function of time. A pre-dispersion of unencapsulated and encapsulated activated carbon particles (activated carbon concentration of 2 g/l) was made by mildly stirring encapsulated or unencapsulated activated carbon particles in a solution of 0.1% sodium caseinate (supplied by FrieslandCampina DMV) in tap water. Caseinate was used to facilitate dispersion of the encapsulated activated carbon particles, but was added to the dispersion of unencapsulated activated carbon as well to allow us to solely study the effect of encapsulation. The pre-dispersion was diluted 4 times with a 0.4 g/l toluene solution leading to a toluene concentration of 0.3 g/l and an activated carbon concentration of 0.5 g/l. A relatively high toluene concentration was used to assure that mass transfer limitations in the bulk of the solution did not determine the adsorption kinetics. The resulting dispersion (100 ml in 100 ml Schott bottles) was mildly stirred and at 3 points in time 5 ml samples were taken over a 0.2 μm filter of which the toluene concentration was determined through headspace analysis using GCMS. For the unencapsulated carbon the above procedure was also applied to determine the amount of toluene adsorbed after 6 h (after which time the toluene concentration has become constant i.e. it has reached equilibrium) as a function of the