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Morphology Study of the Adsorbent from Waste Eggshell by Scanning Electron Microscopy Combined with Fractal Analysis and Adsorbent Regeneration

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Abstract: *As an abundant bio-based renewable material, waste eggshell (WES) is useful to adsorb heavy metal ions from water, but its structure features and performance of reuse lack deep understanding. For the first time, based on scanning electron microscopy (SEM) study, fractal theory was applied to reveal the pore structure feature of waste eggshell and its self-similarity was described in terms of fractal dimension. Taking Cu(II) ion as a typical heavy metal ion, by experimental comparison, the used WES can be better regenerated by NaCl solution without adsorbent loss than by EDTA solution.*

Keywords: *Fractal analysis; Reuse; Waste egg shell; Adsorbent; Heavy metal ion*

1. Introduction

As an abundant bio-based renewable material, waste eggshell (WES) is commonly found as a kind of solid waste from households, restaurants, bakeries, and hatcheries, and has received much attention due to their potential adsorption properties [1]. In the past years, concerning several different heavy metal ions in water, some researchers had studied the adsorption performance of WES and received fairly good results. Chojnacka et al [2] found that WES had high adsorption capacity for Cr(III) ions removal from aqueous solution. Vijayaraghavan et al [3] confirmed the good adsorption capacity of WES for copper ions by column process. Otun et al [4] reported adsorption of Pb(II), Ni(II), and Cd(II) ions from aqueous solution using powdered WES. Yeddou et al [5] employed WES for iron adsorption and also had good results. However, being a natural and renewable material, no attention has been focused on the unique pore structure of WES although it contributes significantly to the adsorption performance it possesses. Different from artificial porous materials, all the pore channels in WES are interconnected. This is very favorable to mass transfer and maximum use of the whole inner surface during adsorption process. In this regard, in this study we focus on the morphology of WES by means of scanning electron microscopy coupled with fractal analysis in order to find out if self-similarity does exist with the pore structure of WES. Subsequently, in view of the importance of the repetitive use of WES, taking Cu(II) ion as a typical heavy metal ion, we evaluated the effects of two solutions of NaCl and EDTA in regenerating WES.

Fractal theory, proposed by Mandelbrot, has been attracting the interest of global researchers from varying areas[6]. The primary objective of this theory is to describe a great variety of natural self-similar structures, which are irregular, rough or fragmented, and exhibit irregularities of various sizes bearing a special scaling relationship to one another. Fractal geometry characterizes the scaling structure of a surface by a number D, called the fractal dimension, which can range from 2, when the surface is smooth, up to 3. The field of fractal is a subject for intensive research and has increasing applications in many categories. In view of the fact of the excellent performance of natural materials in some aspect including adsorption, it is necessary to understand the structure of the natural materials so as to shape and optimize the direction of artificial analogues. We believe knowledge about the pore structures of WES, i.e. learning from nature, may foster rational design and development of new adsorbent materials with desirable high performance, and understanding of the regeneration of the used adsorbent is helpful to the sustainable use of the resource.

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2. Experimental

2.1. Materials

All the chemicals in the experiments were of analytical grade, purchased from commercial sources in China, and used without further purification unless specified otherwise. Stock solution of the copper was prepared by dissolving copper nitrate trihydrate ($Cu(NO_3)_2·3H_2O$) in deionized water, then diluted to obtain the series of standard copper solution for sodium diethyldithiocarbamate spectrophotometry, and aqueous solutions containing different concentrations of Cu (II) for adsorption experiments. The pH of the solutions was adjusted by diluted aqueous solutions of HNO_3 and NaOH. WES was provided free by the canteen at Qingdao University of Science and Technology, China.

2.2. Adsorbent Preparation

WES collected was rinsed several times with tap water to remove impurity, then crushed and boiled with alkali solution containing NaOH content of 8% for 3 h in a pot, with alkali solution being yellow, indicating that eggshell membrane had been dissolved. Subsequently, WES was first soaked in tap water for 7 h, next washed with deionized water to remove alkali solution completely, and then dried at about 100 °C in the dry oven. Finally, WES with diameters of 0.25-0.42 mm (60-40 mesh) was obtained after ground and separated through the test sieves.

2.3. Characterization of WES

Scanning electron micrographs of WES absorbent were taken on a scanning electron microscope (SEM, S-570, Hitachi, Japan). The fractal dimensions of each layer of WES were determined by the box dimension method [7]. The SEM (scanning electron microscopy) micrographs of layers were processed into 256 × 256 × 8 bit digital images by scanner and image processing software. Then, the gray scale of the digital images was taken as the 3rd dimension information, a 256 × 256 × 256 cubic box was established. Covered boxes and gray scales of every box were counted and fractal dimensions were calculated using the following equation proposed by Huo et al [7]:

$$D = \frac{\lg \sum_{i=0}^{255} \sum_{j=0}^{255} B_{ij}}{\lg 255} \tag{1}$$

Where B_{ij} represents the grey scale of the digital image.

2.4. Adsorption and Regeneration Experiments

The Cu (II) concentrations in the solutions were analyzed with sodium diethydlthiocabamate spectrophotometric method, and calibration curve of Cu (II) was shown in Figure 1.

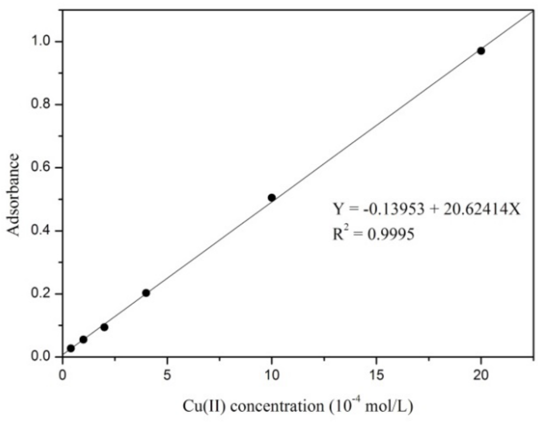

Figure 1: Calibration curve of absorbance vs. Cu (II) concentration

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All experiments were carried out in a thermostatically controlled rocking bed at 220 rpm using 250 mL conical flasks containing 100 mL solution of different Cu (II) concentrations by using batch method due to its simplicity and reliability. Known amount of WES adsorbents was added to 100 mL Cu (II) solution, all the conical flasks were sealed with silicon caps to minimize evaporation. After certain time of agitation, the WES was removed by filtration through a 0.45 μm membrane filter. All experiments were repeated three times.

The Cu (II) removal efficiency and adsorption capacity were calculated by the following equations (2) and (3) respectively:

$$Adsorption(\%) = \frac{C_0 - Ce}{C_0} \times 100\% \tag{2}$$

Where C_0 is the initial Cu^{2+} concentration (mol/L), C_e is the final or equilibrium Cu^{2+} concentration (mol/L).

Regeneration experiments were performed in stirred reactor using EDTA and NaCl solutions as desorbing agent, respectively. Taking Cu^{2+} as a typical heavy metal ion, desorption of Cu^{2+} from the Cu^{2+}-saturated WES was initiated by rinsing with deionized water to remove residual Cu^{2+} on the WES, and followed by mixing and agitating 1.2 g WES with 100 mL EDTA or NaCl solution for the set time. Subsequently, WES was rinsed again with deionized water to remove any trace EDTA or NaCl solution, and then added into Cu^{2+} solution for the next adsorption cycle, with adsorption conditions identical to those of initial adsorption. The desorption-adsorption cycle was repeated using the same WES, and the performance of desorption was evaluated by the subsequent adsorption with Cu^{2+} removal efficiency.

3. Results and Discussion

3.1. Morphology of WES

Eggshell typically consists of ceramic materials constituted by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer. SEM micrographs of the three layers of WES were shown in Figures 2-4, and the presence of numerous micropores in all three layers was observed from these SEM micrographs, which was consist with results found by Tsai et al. and Ok et al [8, 9]. The existence of these numerous micropores in three-layered structure made it possible for WES to exhibit excellent adsorption performance.

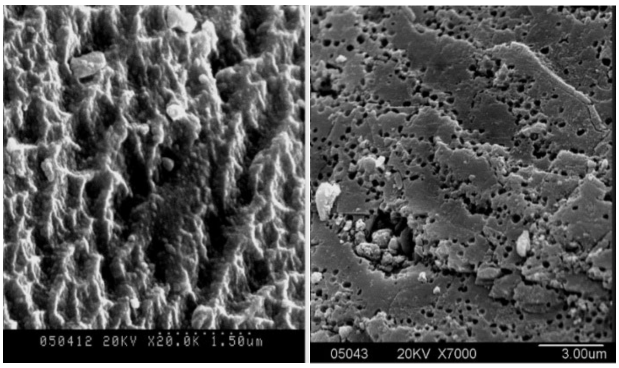

Figure 2: SEM photographs of cuticle on the outer of WES

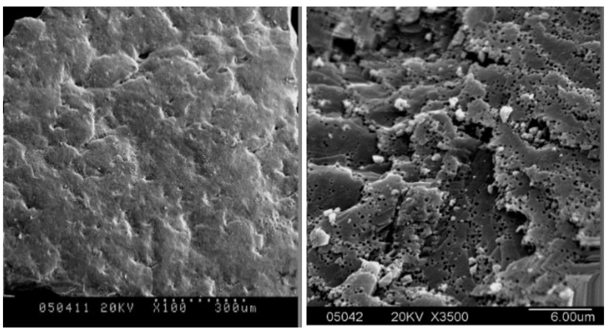

Figure 3: SEM photographs of spongy layer of WES

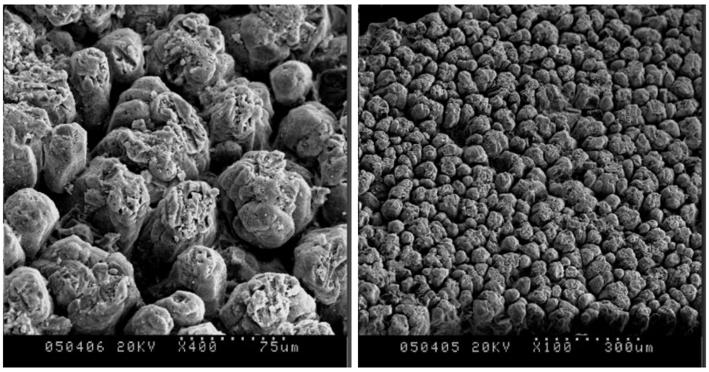

Figure 4: SEM photographs of inner lamellar (or mammillary) layer of WES

3.2. Fractal Dimension of WES

The fractal dimension values of each layer of WES in Figures 2-4 were calculated according to equation (1). The resultant fractal dimensions were showed in Table 1. It can be observed that the fractal dimension values of each layer of WES at different scales approached to 2.80, indicating that WES has fractal characteristics and self-similarity does exist with its pore structure. This proves that WES possesses an ideal distribution of pore structures [10], which cannot be concluded with SEM observations only. The larger specific surface (D>2.5) enables WES to exhibit excellent adsorption performance.

Table 1: The fractal dimension of each layer of WES

Layer		Magnification	Fractal dimension
Cuticle layer		20000	2.849
		100	2.841
Lamellar layer	Mammillary layer	100	2.827
	Top of mammilla	400	2.812
	Root of mammilla	400	2.809
Spongy layer		3500	2.807
		7000	2.810

3.3. Performance of Regeneration

In the beginning, the WES sample was pre-saturated with Cu (II) ion. The desorption-adsorption cycle was repeated using the same WES sample. The adsorption efficiency of each desorption-adsorption cycle was recorded.

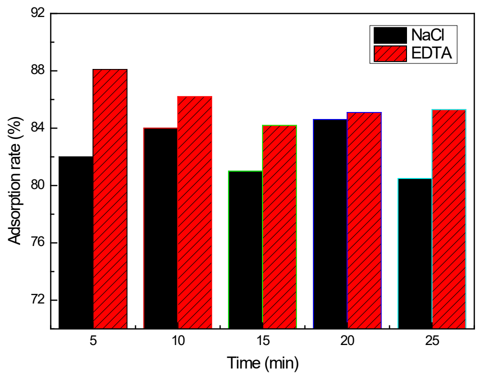

Figure 5: Adsorption efficiency of Cu (II) by regenerated WES. Concentrations for EDTA solution and NaCl solution are 0.05 mol/L

Performance of WES regenerated by EDTA solution is a little better than that by NaCl solution (Fig.5). However, during the process of Cu (II) desorption from WES in EDTA solution, we found a lot

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of fine bubbles (CO_2) releasing from the surface of WES. Compared with the original WES, the reclaimed WES after desorption reduced markedly in weight. This is due to the reaction between EDTA and the $CaCO_3$ in WES, producing CO_2 and meanwhile leading to the elution of calcium species. Although the used WES can be regenerated by EDTA solution, its weight loss is unacceptable. So, we proceed with NaCl solution only.

Further experiments with NaCl solutions of 0.1 and 0.5 mol/L showed accordingly increased performance of WES regeneration (Fig.5 Cycle 2 and Cycle 3). The effect of 0.1 mol/L is favorable since it is closer to that with 0.5 mol/L. As a whole, good regeneration effect of WES can be achieved by desorption in 0.1 mol/L NaCl solution for 10 min. The saturation Cu(II) adsorption capacity of WES before and after regeneration varies between 0.50 and 0.47 mg/g.

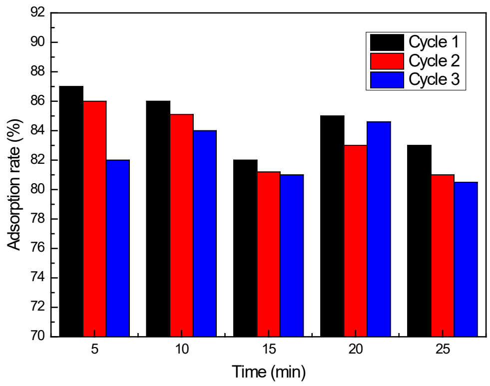

Figure 6: Adsorption of Cu (II) by WES in desorption-adsorption cycles. WES regenerated by: NaCl solutions of 0.5 mol/L (cycle 1); 0.1 mol/L (cycle 2) and 0.05 mol/L (cycle 3), respectively.

4. Conclusion

(1) The pore structure of WES was studied by SEM observation and fractal analysis. WES has fractal characteristics and self-similarity does exist with its pore structure.

(2) The used WES can be effectively regenerated by EDTA or NaCl solution.

(3) Compared with EDTA, NaCl has favorable effect on WES regeneration without loss of the adsorbent.

Acknowledgements

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