ENHANCING WATER SOFTENING PERFORMANCE IN CAPACITIVE DEIONIZATION BY USING ACTIVATED WASTE COFFEE GROUND ELECTRODE

● TRINH NGOC TUAN

ABSTRACT:

This study is to analyze the use of activated waste coffee grounds (WCG), a highly effective electrode material, in the capacitive deionization (CDI) process for the first time. Simply via thermal activation, the WCG's properties were significantly improved, including large surface area and good electrochemical activity. Along with other advantages, such as easy availability, cost effectiveness, and eco-friendly, the WCG could be considered as promising electrode material for CDI units. The hardness removal capacity of WCG electrodes reached 4.4 mg g^{-1} at an applied voltage of 1.5 V. This result is better than most conventional activated carbon materials that are being used in water softening technology.

Keywords: Capacitive deionization, water softening, waste coffee grounds, as-prepared waste coffee grounds.

1. Introduction

Hard water has numerous mineral components, including iron, manganese, calcium, and magnesium. Hardness ions are responsible for serious failures to industrial, domestic, and natural water, such as pile blocking, membrane clogging, and efficiency decay of heaters and heat exchangers [1]. Various methods have been used to remove these impurities. Examples of these include ion exchange [2], electrodialysis [3,4], water acidification, and chemical precipitation [5]. However, these processes also involve the addition of chemicals into water, and most of these chemicals are deleterious for human health and prohibited in drinking water.

As a result, capacitive deionization (CDI) was developed to remove charged ionic species such as salt ions from salty water [6]. The basic concept of CDI is to force charged ions toward oppositely polarized electrodes by imposing a direct electric field forming a strong electrical double layer and holding the ions. Once the electric field disappears, the ions are instantly released back to the bulk solution. In a configuration of CDI cells, the feed stream flows between each pair of high capacity electrodes, that is porous carbon electrodes. By polarizing both electrodes, the charged ions are adsorbed on each electrode surface, and positively charged ions are attracted to the surface of the negatively charged electrode and vice versa [7]. As CDI is a simple system with high ion adsorption capacity, it is potentially an alternative softening water technology with low-energy consumption.

To optimize the operation of the CDI process, carbon materials are usually used as electrodes. They include conventional activated carbon [8-11].

carbon aerogels [12], carbon nanotubes [13-15], and graphene [16,17], all of which exhibit excellent electrosorption properties due to their good conductivities, high surface areas, and suitable pore size distribution. However, they are quite expensive on account of the chemicals and machineries required for their fabrication. Therefore, it is very important to find an abundant and environmentally friendly material that can be applied in the water softening process.

In this study, we demonstrated the possibility of using waste coffee grounds (WCG) as highly effective electrodes, for the first time in CDI systems. Waste coffee grounds are the residues of coffee after grinding and brewing. Given the constant drastic increases in coffee consumption around the world, enormous amounts of WCG without any treatment or recycling method are discarded into the environment. Only negligible quantities are used as fuel in a carbon fuel cell technology [18], distributed to the public for gardening and composting, as they possess high amounts of potassium, phosphorus, copper, and magnesium [19], applied in supercapacitors [20], or utilized to produce biodiesel and ethanol [21]. Our simple thermal treatment, WCG, led to a significant increase in surface area and electrochemical activity, making it suitable for electrosorption of hardness ions. As a result, WCG exhibited considerably higher CDI performance than most current activated carbon materials and appeared to be a promising electrode material for water softening process.

2. Material and methods

2.1. Preparation of Waste coffee grounds

Waste coffee grounds (WCG, obtained from Tanay Hills Coffee Beanery, Hazelnut Arabica, Philippines) were dried at room temperature for three days and put in an oven at 50 oC until the relative humidity dropped below 50% Then, they were sieved to select the powder grains with an average uniform size of 500-1000 μm. Five gram of WCG were baked in a Box Furnace at 950 oC for three different durations of 30, 60, and 90 min and denoted as WCG-30, WCG-60, and WCG-90, respectively. In this step, the carbonization process occurred and WCG changed its structure, making the components more suitable for CDI test. To prevent the combustion of WCG during thermal treatment, it was air-sealed using a ceramic lid.

Finally, WCG was washed with DI water and dried to completely remove its humidity.

2.2. Electrode preparation for CDI test

WCG and PVdF (Polyvinylidene fluoride) as binder (ratio 9:1) were used to fabricate the electrode. Each graphite sheet electrode was 100 mm width × 100 mm length × 0.21 mm thickness To achieve secured adhesion between the carbon mixture and graphite layer, WCG was grounded smoothly and the raw mixture of powders (WCG, PVdF powder, and N-Methyl-2-pyrrolidone solvent) was sonicated and stirred for 24 h, and then coated on the graphite sheet by Dr. Blade equipment. The electrodes were dried in an oven at 60 oC for 12 h to completely remove humidity, and then placed into a vacuum furnace at 70 oC for 24 h to evaporate residual organic materials. Finally, the electrodes were assembled into a CDI device for testing. A hardness water solution was pumped into the CDI system, where the voltage was applied. The dilute solution flowing from the CDI cell was measured every 10 seconds by a conductivity meter. The regeneration process was conducted by turning off the power supply. The ions adsorbed on the electrode surface were desorbed back into the stream flow.

2.3. Experimental Analysis

The artificial feed solution was prepared by dissolving 28.8 mg L-1 of CaCl2, 22.0 mg L-1 of MgSO4 7 H2O, and 39.0 mg L-1 of NaHCO3 in DI water. This feed solution was used for all the experiments in this study, and their total hardness and conductivity of the solution were 35 ppm (as CaCO3) and approximately 110 μS cm-1, respectively. Surface analyses of WCGs were studied by scanning electron microscope (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectrometry (EDX) and X-ray diffraction (XRD). The Brunauer-Emmet-Teller (BET) surface area and pore size distribution (PSD) were examined using nitrogen as an adsorbate at 77 K. The electrochemical performances of as-obtained electrodes were also evaluated by cyclic voltammetry (CV) at room temperature.

3. Results and discussion

3.1. Waste coffee ground characterization

To investigate the morphology and crystal structure of the samples, scanning electron microscope (SEM) and transmission electron

microscopy (TEM) were performed. As seen in Fig. 1a, the WCG has a honeycomb-shaped structure. The composition of WCG consisted of volatile matter (84.86%), fixed carbon (13.85%), and ash (1.29%), measured by the method in ASTM D3172. Following the thermal treatment, their organic compounds were broken up and converted into inorganic components; and the volatile compounds were removed, resulting in the honeycomb walls becoming thinner. Longer holding times for heat treatment resulted in narrower comb walls. Thus, it was expected that the densities of the samples decreased while their specific surface area increased, which would positively affect the ion adsorption process in the CDI cell.

Fig. 1 also displayed the TEM images of the pristine and as-prepared WCGs. As shown, pristine WCG had a sheet structure consisting of several layers. Due to the small amounts of metal elements in comparison with carbon, the metal elements were not observed on the sheet surface. Following the treatment, small particles appeared in each WCG layer, demonstrating the significant change in its composition. The particles could be recognized more discernibly when the duration of heat treatment was increased (from 30 to 90 min). Possibly, the numerous holes and pores were formed on the surface of WCG, consequently enhancing its specific surface area. This result was corroborated by BET measurements, described later in this study.

The energy dispersive X-ray spectrometry analysis (EDX) of the pristine and treated WCG mainly indicated the presence of carbon (> 90%) and oxygen (> 2%), as seen in Table 1. A variety of other elements (< 2%) were also mainly determined as admixtures (Ca, K, Mg, P, and S). These results indicate that the percentages of these elements in all samples were considerably unchanged after a long period of thermal decomposition. It could be concluded that the only changes in the components of the samples involved the conversion of carbon compounds from organic to inorganic forms, and the removal of volatile matters at high temperature. (Table 1)

The XRD patterns of the pristine and as-prepared WCG were shown in Fig. 2a. As seen in the WCG curve, since the pristine WCG consisted of several organic compounds (such as lignin, cellulose, glucose) with their own unclear peaks, an obvious peak could not be distinguished. Following heat treatment, organic compounds were converted into inorganic compounds such as activated carbon, ash, $KCaPO_4$, CO_2, and H_2O vapor. This change was demonstrated in Fig 2b, with the sample weight being reduced eight-fold following 30 min of thermal treatment. Only $KCaPO_4$ peaks could be seen in the XRD curve of WCG-30. However, for longer durations of heat treatment, $KCaPO_4$ peaks gradually disappeared as this compound was broken into smaller components, as seen in the XRD curve of WCG-90 (Fig. 2).

To investigate the difference in specific surface area and pore size distribution of the materials, the Brunauer-Emmett-Teller (BET) measurement was conducted. As shown in Fig. 3a, the specific surface areas of pristine WCG, WCG-30, WCG-60, and WCG-90 were 0.2, 391.9, 675.3, and 675.1 m^2 g^{-1}, respectively. Initially, the pristine WCG had a small

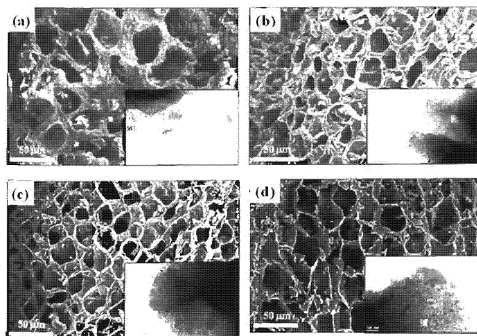*Fig. 1: SEM and TEM (the inset of SEM image) of (a) pristine WCG, (b) WCG-30, (c) WCG-60, and (d) WCG-90*

Table 1. EDX characteristics of pristine and as-prepared WCGs

Element	WCG		WCG-30		WCG-60		WCG-90	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C K	95.29	96 68	95.17	97.43	90.96	93.85	93.63	95.95
O K	4.01	3.05	2.02	1.55	6.73	5.21	4.08	3.14
Mg K	0.18	0.09	0.44	0.22	1.00	0.51	0.80	0.41
P K	0.12	0.05	0.64	0.25	0.12	0.05	0.31	0 12
S K	0.08	0.03	0.16	0.06	0.17	0.06	0.31	0 12
K K	0 04	0.01	0 03	0.01	0.21	0.07	0.01	0.00
Ca K	0 28	0.08	1.55	0.48	0.81	0.25	0.85	0.26
Totals	100.00		100.00		100.00		100.00	

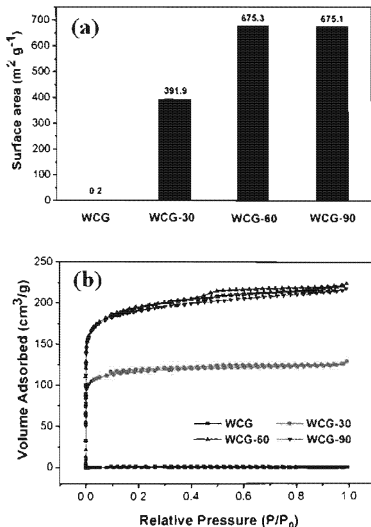*Fig. 2: X-ray diffraction patterns and the weight plot of pristine and as-prepared WCGs*
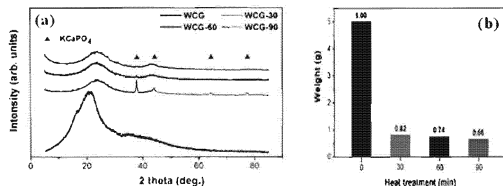
specific surface area, and it was increased remarkably via thermal treatment. The maximum surface area was achieved at 60 min of baking, during which the volatile matters were entirely removed. When prolonging heat treatment duration to 90 min, the activated carbon materials were partly converted to ash; therefore, the surface area was slightly reduced. The specific surface area was known to be a powerful parameter to evaluate the CDI performance. On the basis of the above BET result, as-prepared WCGs were expected to have excellent CDI efficiency. Moreover, Fig. 3b indicated the nitrogen adsorption and desorption isotherms of the pristine and as-prepared WGCs. It was clearly observed that the hysteresis loops of the pristine WCG showed the dominance of the micropore structure with similar adsorption and desorption curves. Following heat treatment, the micropore structure was converted into mesopore form, as shown in the

curves of WCG-30, WCG-60, and WCG-90. The greater duration of thermal treatment resulted in more mesoporous structures, as indicated by the clearer difference between the adsorption and desorption curves. Undoubtedly, mesoporous size distribution was greatly beneficial to ion electrosorption in CDI system [22,23]. (Fig. 3).

A three electrode system at ambient temperature was used to measure electrochemical properties of the materials. The prepared electrodes, platinum plates, and saturated calomel electrodes were used as the working electrode, the counter electrode, and the reference electrode, respectively. The potential sweep cyclic voltammetry (CV) measurement was carried out in 0.1 mol L⁻¹ KOH solutions at a scan rate of 100 mV s⁻¹. It should be noted that the specific capacitance was proportional to the average areas of CV curves, and that higher capacitance implied that more electrolyte ions were able to reach the pores of electrodes. As seen in Fig. 4, pristine WCG showed no electrochemical activity with a very narrow CV curve. After heat treatment, its activity considerably improved with a significantly extended curve. Upon increasing the duration of thermal process to 60 min, the capacitance

3.2. CDI unit cell performance

The electrosorption capacity (in mg g^{-1}) is defined as the adsorbed ion amounts per gram of the electrode and can be examined by the concentration or conductivity variation of solutions during the charging process. The CDI unit cell performance was conducted to evaluate the ion removal ability of the electrode. The conductivity of the feed solution was approximately 110 μS cm^{-1}.

As discussed above, the pristine WCG showed no surface area and electrochemical activity. Hence, it was not necessary to apply it to the CDI test. Fig. 5 showed the adsorption and desorption profiles of as-prepared WCGs at different applied voltages (1, 1.5, and 2.0 V). It was shown in Fig. 5 that WCG-60 displayed the best ion removal efficiency and longest adsorption time at every voltage. CDI performance improved and corresponded with the increase in the thermal treatment duration (up to 60 min). However, the efficiency declined with longer heat treatment time, as seen at WCG-90. This was because of the smaller electrochemical conductivity of WCG-90, as compared to that of WCG-60. For instance, at 1.5 V, WCG-30,

increased from 1 to 78 and 128 F g^{-1} corresponding with pristine WCG, WCG-30, and WCG-60, respectively. However, this value decreased to 91 F g^{-1} at 90 min of heat treatment, since the activated carbon in WCG was partly disintegrated to ash with low electrochemical activity. Moreover, no peak could be found in the CV curves, suggesting that ions were adsorbed on the electrode surface by forming an electric double layer of Coulombic interaction, as opposed to an electrochemical reaction. Based on the excellent capacitance of WCG-60, this sample was predicted to have the best CDI performance among all the as-prepared electrode materials. (Fig. 4).

Fig. 4: CV curve of pristine WCG and as-prepared WCGs at the scan rate of 100 mV s^{-1} in 0.1 M KOH solution
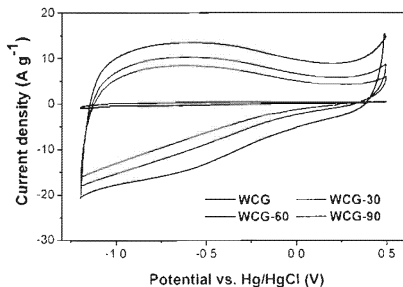
WCG-60, and WCG-90 showed CDI efficiencies of 20%, 39%, and 26%, respectively. The maximum CDI efficiencies that could be achieved were 4.4 mg g^{-1} at 1.5 V and 6.8 mg g^{-1} at 2.0 V using WCG-60. This result was in good agreement with the excellent properties of WCGs, described previously in this article. Noticeably, the ion adsorption efficiency of as-prepared WCG was better than most activated carbon electrodes at the same applied voltage (2.0 V), such as graphene (1.8 mg g^{-1}) [23], carbon nanotube (0.75 mg g^{-1}) [24], or reduced graphite oxidate-resol (3.2 mg g^{-1}) [25]. (Fig. 5).

Fig.5: Cyclic test (a) first cycle and (b) all cycles of WCG-60 at 1.5 V with a flow rate of 10 mL min-1 and the feed solution of 180 ppm (as CaCO₃)

(a)

(b)
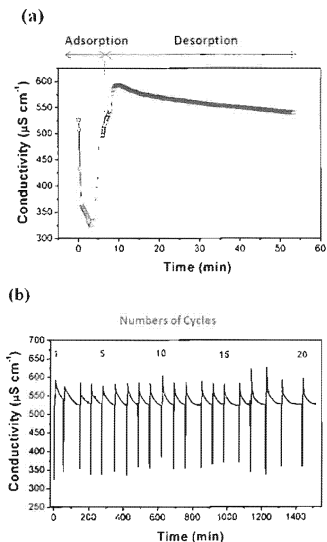
The cyclic test was performed to evaluate the stability of the WCG-60 electrode in the CDI unit. This factor played a decisive role with respect to the practical feasibility of this material. In this case, the concentration of feed solution was increased to 180 ppm (initial conductivity of 540 μS cm^{-1}), similar to the characteristics of hard water in natural conditions. Every 10 min of adsorption followed by 40 min of desorption was implemented at 1.5 V with a flow rate of 10 mL min^{-1} (Fig. 6a). The experiment was repeated 20 times in continuous operation mode for a total period exceeding 20h (Fig. 6b). As seen in Fig. 6a, the adsorption time was much less than desorption time. The effects of the meso-porous structure with the complicated combination of micro - and meso - pores on the removal pathway of ions can explained this. In the first cycle, the CDI efficiency reached 40%, with a total ion removal of 3.0 mg g^{-1}. As expected, in Fig. 6b, a significant degradation of CDI performance was not observed during 20 cycles. At the 20th cycle, the CDI efficiency remained at 36%, which was only 4% lower than that of the first cycle. Undoubtedly, these results significantly demonstrated the excellent stability of WCG material in the water softening process.

4. Conclusions

In this report, we successfully introduced the excellent as-prepared WCG electrode which has never been used before for CDI test. This material showed outstanding advantages, including high electrochemical activity, large surface area, abundance, and environmentally friendly properties. In particular, its CDI performance was remarkable and stable compared to other conventional activated carbon materials. Moreover, by using a thermal treatment step, the fabrication method of the electrode was simple and inexpensive. In summary, the fabricated material displayed immense potential as a promising electrode material for CDI application in water softening technology ∎

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Author's informations.
Ph.D. TRỊNH NGỌC TUẤN
Faculty of Energy Technology, Electric Power University

NÂNG CAO HIỆU QUẢ LÀM MỀM NƯỚC
TRONG HỆ THỐNG CAPACITIVE DEIONIZATION
SỬ DỤNG ĐIỆN CỰC BÃ CÀ PHÊ

● TS. **TRỊNH NGỌC TUẤN**
Khoa Công nghệ năng lượng,
Trường Đại học Điện lực

TÓM TẮT:

Trong bài báo này, chúng tôi sử dụng bã cà phê (WCG) để chế tạo điện cực hiệu quả cao cho quá trình khử ion điện dung (CDI). Sau khi được hoạt hóa bởi nhiệt độ cao, chất lượng của WCG được cải thiện rõ rệt, bao gồm diện tích bề mặt lớn và hoạt tính điện hóa được nâng cao. Ngoài ra, bã cà phê còn có các ưu điểm khác như rất phổ biến trên thị trường, chi phí nguyên liệu thấp và thân thiện với môi trường. Điều này khiến cho nó trở thành vật liệu chế tạo điện cực CDI rất hứa hẹn. Kết quả nghiên cứu cho thấy hiệu quả loại bỏ độ cứng của WCG lên tới 4,4 mg/g trong điều kiện điện áp 1,5 V. Kết quả này cao hơn hầu hết các vật liệu carbon hoạt tính truyền thống khác đã được nghiên cứu và sử dụng cho mục đích làm mềm nước.

Từ khóa: Capacitive Deionization, làm mềm nước, bã cà phê, bã cà phê hoạt tính.