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Capacitive deionization of a RO brackish water by AC/graphene composite electrodes

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HIGHLIGHTS

- Activated carbon (AC) recycled from palm-shell wastes can be used as capacitive deionization (CDI) electrodes.
- The GAC composite prepared by dispersion of AC in graphene has the main charge storage in the micropores.
- The GAC composite electrode for water recycling from a semiconductor wastewater by CDI has a desired electrosorption efficiency and stability.

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ABSTRACT

A feasibility study for water recycling and reuse of a reverse osmosis (RO) brackish wastewater by capacitive deionization (CDI) was carried out in the present work. Palm-shell wastes enriched in carbon was recycled to yield valuable activated carbon (AC) that has advantages of high surface area, high specific capacitance, and low electrical resistance as the CDI electrodes. The GAC prepared by dispersion of AC in the graphene (rGO) layers has a high surface area and electrical conductivity for CDI. The GAC electrodes have increasing electrosorption efficiencies from 1.6 to 3.0% during the repeated electrosorption-regeneration cycles under $+1.2 \rightarrow 0 \rightarrow +1.2$ V while the efficiencies the AC electrodes decrease from 2.7 to 1.6%. It is clear that the GAC-based electrodes have a better electrosorption efficiency and stability in, for example, the three repeated electrosoption-regeneration cycles for CDI of the wastewater. This work also exemplifies that the AC recycled from biomass such as palm-shell wastes can be used in CDI electrodes for recycling and reuse of wastewater.

1. Introduction

Numerous methods such as chemical precipitation, filtration, reverse osmosis (RO), electrodialysis, physical adsorption, and bio-adsorption have been developed for water recycling and reuse from waste or contaminated water (Gabarron et al., 2016; Gupta et al., 2012; O'Donnell et al., 2016; Ramasamy et al., 2017). Many wastewater treatment plants are using RO for water recycling. Note that the feed water for RO is generally pretreated by biological (to reduce the residual COD) and ultrafiltration processes. The RO brackish wastewater obtained from a semiconductor wastewater stream frequently contains relatively high concentrations of ions, which may not be recycled engineering-feasibly.

Desalination by capacitive deionization (CDI) possessing advantages of low energy consumption and environmental friendly has many applications such as softening water (Laxman et al., 2015; Silva et al., 2016). Ions in water can be removed by electrosorption within the electrode double layers when a potential difference is applied (Dykstra et al., 2016; Farmer et al., 1996). The electrosorbed ions can be released back to solution by removing or reversing the electrical field. Thus the CDI performance is associated with surface and porous characteristics of carbon electrodes involved. Generally porous carbon having a high surface area, good conductivity, and high capacitance is preferred for CDI electrodes (Anderson et al., 2010; Yang et al., 2015). Porous carbon such as activated carbon (AC), carbon aerogel, carbon nanotube, and graphene (rGO) has been widely used in CDI (Porada et al., 2013; Xu et al., 2016).

Oil palm fruit that is mainly produced in Malaysia has been a major source of vegetable oil. Palm-shell is the primary solid waste (heat of combustion = 4200–4600 kcal/kg) in the palm oil

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processing (Hamza et al., 2016). Concentrations of nitrogen, sulfur and phosphorous in palm-shell are relatively low (Adebisi et al., 2017; Hossain et al., 2016). The palm-shell can, therefore, be used as supplementary fuels for power generation. In addition, the palm-shell enriched in carbon can also be recycled for the valuable AC.

Graphene (rGO), a two-dimensional carbon with a hexagonal lattice, was first reported by Geim and coworkers in 2007 (Geim and Novoselov, 2007). With the advantages of good mechanical strength, flexible, good electrical and thermal conductivity, high surface area and transparency, and great disinfection ability, rGO has been widely used in solar cells, touch screen, super-capacitor, and sensors (Novoselov et al., 2012). Li and coworker reported that commercial AC and rGO (20%) electrodes were used for capacitive deionization of diluted NaCl aqueous solution (25 ppm) (Li et al., 2012). In this study, the GAC composite prepared by dispersion of AC (recycled from the palm-shell waste) in rGO was used as the CDI electrodes. Specifically, a feasibility study for water recycling and reuse from a RO brackish wastewater by CDI was carried out.

2. Materials and methods

Activated carbons are generally prepared by chemical and physical activation methods. Briefly, the palm-shell wastes were washed to remove the dust, and grounded and sieved to the size range of 1–73 μm $ZnCl_2$ (Sigma) was used as the activated agent in the chemical activation process (Khadiran et al., 2014). About 10 g of the dried and fine palm-shell wastes and 10 g of $ZnCl_2$ was mixed in 100 mL distilled water at 323 K for 1 h. The slurry then dried at 373 K for 24 h, and carbonized under a nitrogen gas flow (150 mL/min) at 1073 K for 1 h to yield AC. The AC was then washed with 1 N HCl and distilled water for the CDI electrodes.

The graphene oxide (GO) was prepared using the Hummers method. Briefly, about 1 g of graphite flake, 80 mL of sulfuric acid (H_2SO_4, Sigma), 1.6 g of sodium nitrate ($NaNO_3$, Hayashi Pure chemical), and 7.5 g of potassium permanganate ($KMnO_4$, Sigma) were well mixed at 308 K for 24 h. The solution was diluted with 200 mL of deionized water at 353–368 K. The excess potassium permanganate was removed by hydrogen peroxide (H_2O_2, 30–31%, Sigma). The extra metal ions in the solution were washed with 20 mL of hydrochloric acid (HCl, Sigma). The residual acid was washed by deionized water, and centrifuged several times. After dried at 313 K for 2 d, the yielded GO was dispersed in the deionized water (1 mg/mL), and ultrasonicated for 1 h to form the GO solution. Instead of using hydrazine (a highly hazard reductant commonly used in chemical reduction for GO), the green agent hexamethylenetetramine (HMTA) (99%, Alfa Aesar) was used for reduction of GO to yield the rGO.

The AC and rGO at the weight ratio of 10:1 were mixed, and freeze-dried to form the GAC composite. To prepare the CDI electrodes, the AC or GAC was mixed with polyvinylidene fluoride (PVdF), dissolved in dimethylacetamide (DMAc) (GAC (or AC): PVdF: DMAc = 10:1:20), and stirred for 3 h. The homogeneous slurry was coated onto the graphite sheet which was cut into the size of 2.5 2.5 cm^2. The electrode was dried at 353 K to remove the organic solvent.

The electrosorption experiments for the RO brackish wastewater that was obtained from a semiconductor wastewater stream under the voltage of +1.2 or −1.2 V were carried out in a CDI reactor consisted of 14 electrodes. The effective area of each electrode was 6.25 cm^2 (2.5 × 2.5 cm^2). The concentrations of ions in the wastewater were analyzed on an inductively coupled plasma-mass spectrometer (ICP-MS) (Hewlett Packard 4500). The electrosorption efficiency (%) during CDI can be expressed as $(C-C_0)/C_0 \times 100\%$, where C and C_0 (ppm) represent the final and initial concentrations of ions, respectively.

Morphologies of the rGO, AC, and GAC samples were determined by high resolution analytical transmission electron microscopy (TEM) (Jeol, JEM-3010) at the operation accelerating voltages were 200 keV. Molecular rotation and vibrational modes of the AC and GAC were determined by Raman spectroscopy (Horiba Jobin Yvon, LabRAM HR800). For comparison, the characteristic properties of a commercial AC (AC-M) (Goldstar Carbon Tech Inc.) were also studied. Pore characteristics of the AC and AC-M were determined by nitrogen adsorption at 77 K on a porosimeter (ASAP-2000, Micromeritics). The BET surface areas of the samples were calculated from the adsorption isotherms using the Brunauer-Emmett-Teller equation. Elemental analyses of palm-shell, AC, and AC-M were also determined on an elemental analyzer (EA, GmbH).

The electrosorption performance of the electrodes was studied by cyclic voltammetry (CV) (Artism CV-50W) with a three-electrode system. Platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The CV was operated between −0.6 V - 0.6 V at a scan rate of 5 mV/s in a HCl (1 M) solution. The specific capacitance (F/g) can thus be calculated by equation ($C = i/mv$), where C represents the specific capacitance; m and v are the amount of activated carbon (g) and scan rate (V/s), respectively. The electrochemical impedance spectrometer (EIS) was consisted of a three-electrode system using the AC or GAC electrode as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode at the frequency range between 0.1 to 10^5 Hz in a 0.1 M NaCl solution. By applying different frequency alternating current potential with a small amplitude wave, the Nyquist plot and impedance of the electrodes were obtained. The CDI electrosorption efficiencies of the AC electrodes were measured by the determination of changes in electrical conductivity in wastewater.

3. Results and discussion

For water recycling and reuse of the RO brackish wastewater, the rGO, AC (recycled from palm-shell wastes), and GAC composite possessing functions of high surface area and superior conductivity were used as the CDI electrodes. The elemental analysis data for palm-shell and AC are shown in Table 1. For comparison, the characteristic properties of the AC-M is also included in Table 1. It seems that after carbonization to yield the AC, the carbon and hydrogen fractions of the palm shell waste are changed from 48 to 66% and 6.1 to 3.0%, respectively. The carbon in the palm-shell

Table 1
Chemical and physical properties of the AC recycled from palm-shell wastes and commercial AC (AC-M) (for comparison).

	Elemental analysis (wt%)			C/H	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
	N	C	H				
Palm-shell	0.32	48	6.1	0.65			
AC	0.32	66	3.0	1.8	1145	2.1	0.60
AC-M	0.58	71	2.2	2.6	838	2.2	0.46