

Supplementary Information

Resource usage of biomass waste as oak fruit peel to synthesize carbon with graphene oxide-like composition and composite with $Mg_{1-x}Ca_xFe_2O_4$ in removing Cd (II) from water: characterization, magnetic properties, and potential adsorption study

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Materials and Methods

Materials

The oak fruit peel (OFP) was collected from Zagros Mountains in the west of Iran. Standard graphite (99.9%) was obtained from Kanto Chemical Co. Inc., Japan. Hydrogen peroxide (H_2O_2 , 30%), sulfuric acid (H_2SO_4 , 95%), phosphoric acid (H_3PO_4 , 85%), hydrochloric acid (HCl, 37%), Hydrofluoric acid (HF, 48%), potassium permanganate (KMnO_4 , >99%), iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), nitric acid (HNO_3), and metals (Cd, Pb, Co, Ni) standard solutions (1000 mg/L) were purchased from Merck, Germany. Sodium hydroxide (NaOH) was acquired from Sigma-Aldrich Chemical, USA. All chemicals were of analytical grade with the highest purity (>99%).

Preparation of carbon with graphite-like composition

The carbon with graphite-like composition (C_G) was prepared from OFP by carbonization. First, 50 g of OFP was successively cut into small pieces, washed using ultrapure water (UPW), sun-dried for 10 h, and finally completely dried in an oven at 80 °C for 12 h. After that, the OFPs were carbonized in the presence of atmospheric air in a muffle furnace at 400°C (C_G400), 500°C (C_G500), and 550°C (C_G550) for 3 h. The obtained powder was then rinsed three times with UPW and dehydrated in an oven at 70°C for 3 h to obtain C_G . For desilication, 10 g of reasonable C_G sample (i.e. C_G550) was dissolved in 30 ml of HF and stirred at 50 °C for 3 h. The resultant was then collected by centrifugation, washed several times with UPW to raise pH to neutral, and dried at 80 °C for 12 h (termed as C_G550D). The energy used to prepare C_G sample is determined using Eq. (1).

$$Q = (ET)/3.6 \quad (1)$$

Where Q represents the energy utilized (MJ), E represents the power of the oven/furnace (kW), and T indicates the duration of heat.

Preparation of carbon with graphene oxide-like composition

Carbon with graphene oxide-like composition (C_{GO}) was fabricated from as-prepared C_G (i.e. C_{G550D}) using a simple room temperature method.¹ In detail, 320 ml of H_2SO_4 and 80 ml of H_3PO_4 were mixed successively with 3 g of C_{G550D} under magnetic stirring. 18 g of $KMnO_4$ was then slowly added over a period of 10 h. After that, the mixing procedure was extended for 5 more days to permit the oxidation of C_{G550D} . Next, 60 ml of H_2O_2 (dropwise) was added to the solution to terminate the reaction, causing a color change from black to light brown. The resulting mixture was centrifuged and the resultant was washed with 1M HCl for 3 times and UPW several times to raise pH to neutral. The final product was dried in an oven at 70°C for 12h.

Synthesis of Ca-substituted $MgFe_2O_4$

The details of the preparation and characterization of $Mg_{1-x}Ca_xFe_2O_4$ (MCF) nanomaterials can be found in a previous publication.² Briefly, $Mg_{1-x}Ca_xFe_2O_4$ with x values of 0.2 (MCF2) and 0.8 (MCF8) were fabricated by sol-gel method. The metal nitrates (i.e. $Fe(NO_3)_3 \cdot 9H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$) and $C_6H_8O_7 \cdot H_2O$ in the ratio of 1:1 were weighted and mixed with an appropriate volume of UPW. The mixture was stirred at 360 rpm for 3 h at 50°C. Then, the heating process was continued for more than 2 h at 80°C to obtain a dark brown powder. The resultant was annealed in a Heraeus M110 muffle furnace (Heraeus Holding GmbH, Hanau, Germany) at 1000 °C for 4 h to obtain a pure phase of MCF.

Fabrication of C_{GO}/MCF nanocomposites

The C_{GO}/MCF nanocomposites were prepared using a one-step hydrothermal method. Briefly, 30 mg of C_{GO} was sonicated (Elma E 30H Elmasonic, Germany) for 2 h in 20 ml of UPW to obtain a homogenous carbon solution. Next, 30 mg of MCF nanomaterials was dissolved in 20 ml of UPW and sonicated for 2 h. After that, the carbon solution was gradually added to the MCF solution. The mixture was then kept in a shaker (IKA-KS 130 basic, Germany) at ambient temperature at 400 rpm for 3 h. The resulting mixture was transferred to a 50 ml hydrothermal reactor at 150 °C for 3 h. After cooling naturally to ambient temperature, the resultant was collected by centrifugation, rinsed with UPW for several times, and dried in an oven at 70 °C for 12 h. Fig. S1 presents a schematic flow sheet for the synthesis of C_{GO} from OFP waste, MCF nanomaterials, and C_{GO}/MCF nanocomposites.

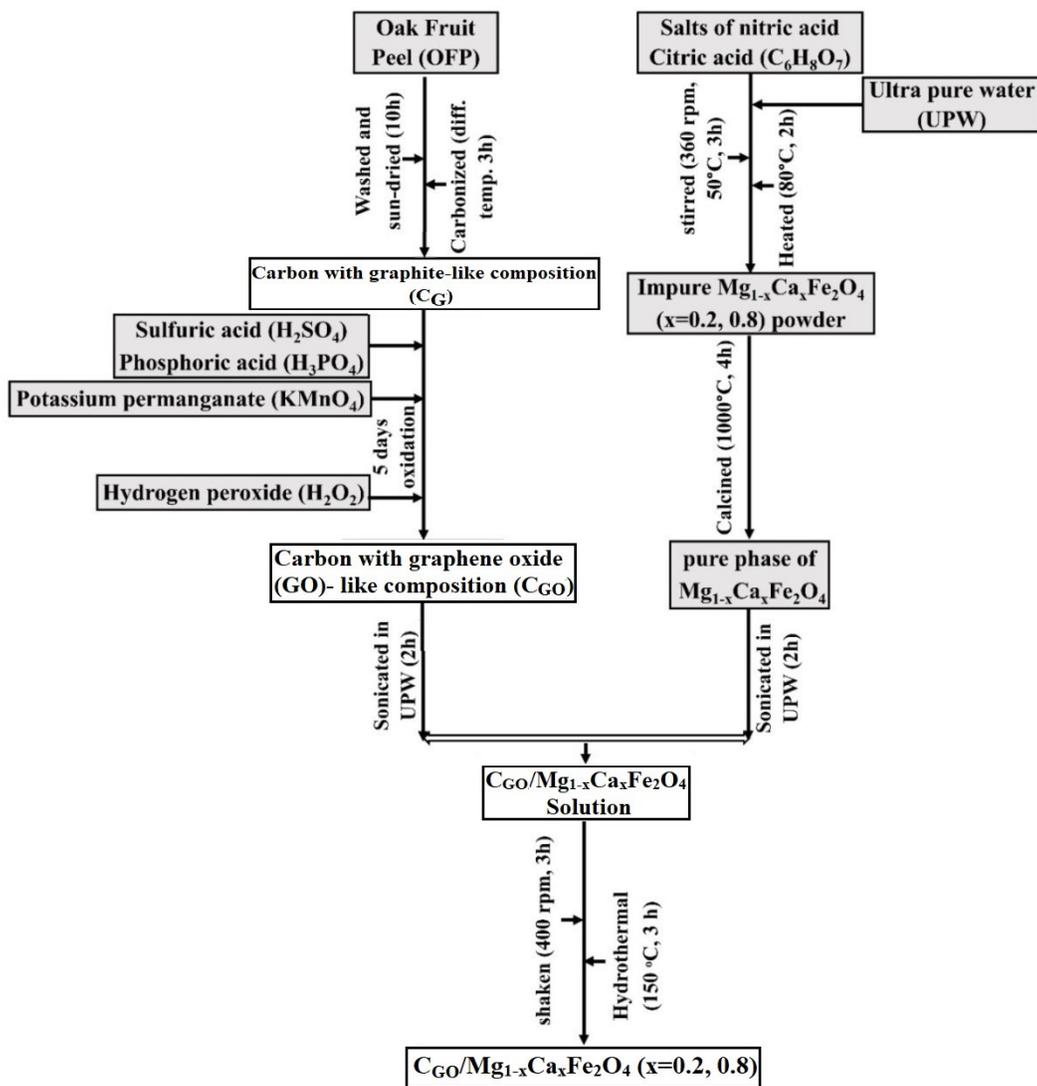


Fig. S1 Schematic diagram for the synthesis of C_{GO} from OFP waste, MCF nanomaterials, and C_{GO}/MCF nanocomposites.

Characterization

The C_{GO} and C_{GO}/MCF nanocomposites were characterized by X-ray diffraction patterns (XRD) (Rigaku, model Ultima IV, Cu K-alpha: 1.5418 Å, Japan), Raman Spectroscopy (RS) (TakRam N1-541, Teksan Co, Iran) with laser exciting at 532 nm, Fourier-transform infrared spectroscopy (FTIR) (Bruker, model Tensor 27, Germany), X-ray photoelectron spectroscopy (XPS)

(EA10, BESTEC Co., Germany) with Al K α (E = 1486.6 eV) radiation, field emission scanning electron microscopy (FESEM) (Zeiss Sigma 300-HV, Germany), and Transmission Electron Microscopy (TEM) (Carl Zeiss-EM10C-100Kv, Germany) at accelerating voltage 100 Kv). The specific surface area and pore size distribution were obtained utilizing a N₂ isothermal adsorption tester (BELsorp, model mini II, Japan) at 77 K and estimated by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The magnetic properties of as-prepared C_{GO}/MCF nanocomposites were attained at room temperature using a Vibrating-Sample Magnetometer (VSM) (Weistron, model VSM1100, Taiwan). The surface charges of prepared C_{GO}/MCF nanocomposites were determined by measuring the point of zero charges (pH_{pzc}) for electrostatic attraction analysis. The pH_{pzc} of as-prepared C_{GO}/MCF nanocomposites was determined using the method reported by Dao et al.³ Herein, 10 mg of nanocomposite was put into 20 mL NaNO₃ solution with a concentration of 0.1 M. The amount of different initial pH (pH_{initial}) (from 3 to 8) was adjusted using HCl 0.1 M or NaOH 0.1 M solutions. The attained solution was shaken for 48h and then the final pH value (pH_{final}) was measured by a pH meter (WTW, model 323, British- U.S.A). The pH_{pzc} could be determined from the curve of $\Delta\text{pH} = \text{pH}_{\text{final}} - \text{pH}_{\text{initial}}$ versus pH_{initial}.

Experimental approach

All adsorption experiments were performed in batches on a shaker operating at 480 rpm at ambient temperature. The aqueous solutions containing metal ions were prepared by diluting the metal stock solutions with UPW. Here, the pH value in solutions was estimated to be ~2 since the standard solutions were acidic in nature. The initial pH of the solutions was adjusted to 7 by adding NaOH (1 M) solution before mixing with the adsorbent using a pH meter (WTW, model 323, British-U.S.A). Accordingly, a set of 250 ml Erlenmeyer flasks containing 50 mL of metal

solutions were used in adsorption studies.

The adsorption capacity of Cd²⁺ by C_{GO}/MCF nanocomposites was evaluated at different contact times (1-60 min), C_{GO}/MCF nanocomposite doses (0.002-0.01 g), and initial Cd²⁺ concentrations (5 to 60 mg/L). The effects of coexisting ions, including Pb²⁺, Co²⁺, and Ni²⁺, on Cd²⁺ adsorption onto reasonable adsorbent (i.e. C_{GO}/MCF2) were assessed at a contact time of 20 min, a C_{GO}/MCF2 dose of 0.003 g, and an initial Cd²⁺ concentration of 10 mg/L. The coexisting ions were added to the solution in a composite form, each at a concentration of 10 mg/L.

Further, the C_{GO}/MCF2 adsorbent was examined in real wastewater collected from a local plated metals restoration workshop (Tehran, Iran). The wastewater sample was collected in a plastic container and stored at 4 °C in the refrigerator. The sample was then utilized for the experiment without any pre-treatment on the next day. The initial analysis of the wastewater sample revealed the existence of Cd (5.7 mg/L), Pb (2 mg/L), Zn (5.1 mg/L), and Fe (50.1 mg/L) metals, and pH was obtained to be 7. Herein, the experiments were performed in two stages under the following conditions: contact time of 20 min and C_{GO}/MCF2 dose of 0.003 g. First, C_{GO}/MCF2 adsorbent was employed to adsorb metals in 20 ml wastewater, and subsequently, the metal removal efficiency was assessed. Second, the effluent from the first stage of the experiment (10 ml) was treated with a fresh C_{GO}/MCF2 adsorbent.

The adsorbents were separated from the contaminated solutions using an external magnet. The metal ion concentrations in the solutions were assessed using a Flame Atomic Absorption Spectrometer (Varian, model AA 240FS, U.S.A). The adsorption capacity (q_e , mg/g) of Cd (II) on as-prepared C_{GO}/MCF nanocomposites was determined by the Eq. (2):⁴

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (2)$$

Where C_0 (mg/L) is the initial and C_e (mg/L) is the equilibrium concentration of Cd (II), V (L)

is the volume of the Cadmium solution, and m (g) is the mass of C_{GO}/MCF nanocomposites.

All adsorption experiments were conducted in triplicate to ensure data reproducibility, and the average results have been reported. Besides, blank samples (without adsorbent) were also run in parallel during the batch experiments, and the recorded concentration at the end of each operation was taken the same as the initial one.

Regeneration study

The adsorbent reuse investigation was carried out with 10 mL HCl (0.2 M) solution at ambient temperature.⁴ The solution was shaken at 480 rpm for 30 min. The adsorbents were then rinsed using ultra-pure water several times until the pH was around 7, and dried at 80°C in an oven. This experiment was employed for three adsorption cycles of Cd^{2+} onto C_{GO}/MCF nanocomposites under our experimental conditions (contact time=20 min, pH =7, nanocomposite dosage= 0.004 g, initial Cd^{2+} concentration= 10 mg/L, volume solution= 50 ml).

Adsorption kinetics and isotherms

To comprehend the rate of Cd (II) adsorption onto nanocomposites, adsorption type (monolayer or multilayer), as well as its mechanism, it is required to analyze the adsorption kinetics and isotherms. The obtained adsorption data were analyzed by the pseudo-first-order (Eq. (3)) and pseudo-second-order (Eq. (4)) kinetics, the Langmuir (Eq. (5)) and Freundlich (Eq. (6)) isotherms models.⁴

$$\log \frac{q_e}{q_e - q_t} = \log q_e - K_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L X_m} + \frac{C_e}{X_m} \quad (5)$$

$$\text{Log} q_e = \text{Log} K_f + \frac{1}{n} \text{Log} C_e \quad (6)$$

Where q_e (mg/g), q_t (mg/g), K_1 (Lmin⁻¹), K_2 (mg. min g⁻¹), C_e (mg/L), X_m (mg/g), K_L (Lmg⁻¹), K_F (mg/g) and $1/n$ represent adsorption capacity of Cd (II) at equilibrium time, adsorption capacity at t(min) time, the pseudo-first order adsorption rate constant, the pseudo-second order adsorption rate constant, the equilibrium adsorbate concentration, maximum adsorption capacity, Langmuir constant, Freundlich constant (adsorption capacity) and intensity of adsorption, respectively. K_1 and q_e were calculated using the slope and intercept of $\text{Log} (q_e - q_t)$ vs. time curves. K_2 can be derived from the intercept and slope of the t/q vs. t plot. The Langmuir isotherm (Eq. (5)) fundamentally presupposes that the adsorbent surface is homogeneous, that energy-equivalent active sites are dispersed nearly evenly. In this isotherm, the values of X_m , and K_L were determined from the slope and intercept of C_e/q_e vs. C_e . According to the Freundlich isotherm, (Eq. (6)) sorption occurs on heterogeneous surfaces. It is feasible to determine K_f and $1/n$ from an intercept and slope of a linear plot of $\log (q_e)$ vs. $\log (C_e)$.³ Another important factor is the separation factor of equilibrium (R_L), which is used to assess the favorableness of the adsorption process (Eq. (7)):

$$R_L = \frac{1}{1 + C_e K_L} \quad (7)$$

The reversible, favorable, linear, and unfavorable adsorption are respectively denoted by the values $R_L = 0$, $R_L < 1$, $R_L = 1$, and $R_L > 1$.

Results and discussion

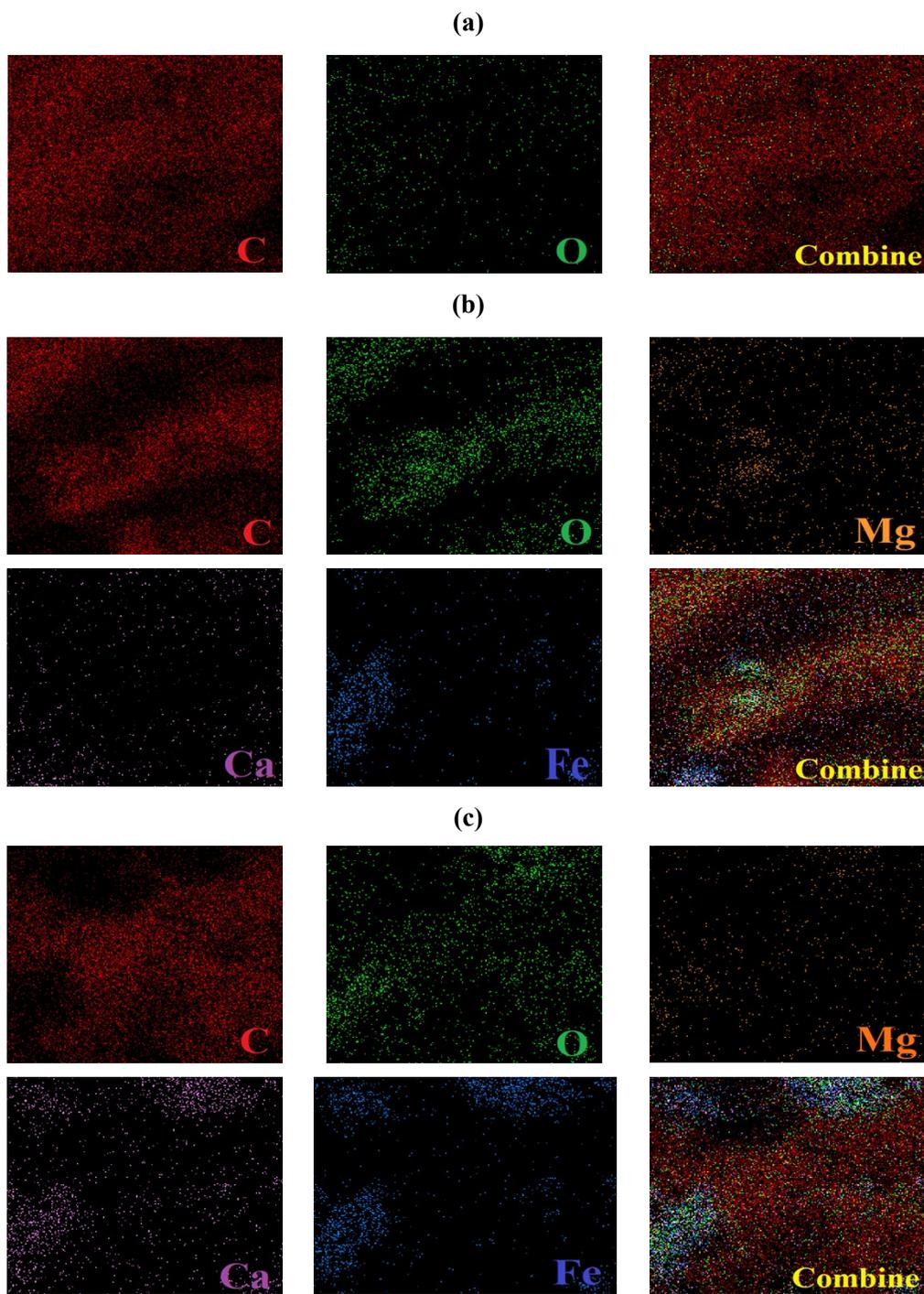


Fig. S2 EDX-Mapping of (a) C_{Go}, (b) C_{Go}/MCF2, and (c) C_{Go}/MCF8.

The morphological features of C_G and standard graphite were compared by SEM analysis (Fig. S3a-i and b-i). Both samples displayed irregular flake-like morphologies. The particles within these structures range from 0.09 to 0.50 μm in size. The EDX analysis indicated that carbon was the predominant element in both C_G and standard graphite samples. Meanwhile, the C_G had slightly higher levels of this element compared to standard graphite. The C_G and standard graphite had carbon contents of around 81% and 78%, respectively. The elevated carbon content in the C_G could be due to a great quantity of carbon-rich material presented in the precursor OFP waste. This could impact the ability of C_G to be used as a valuable starting material for the preparation of C_{GO} .

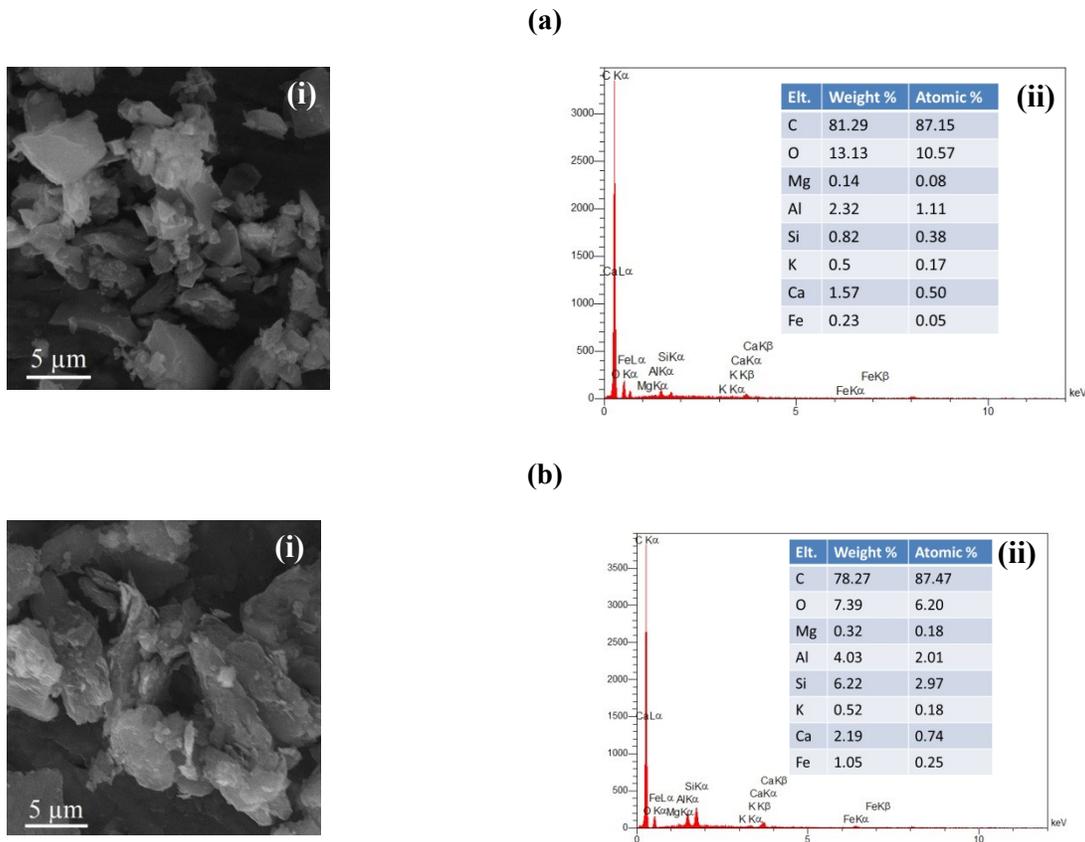


Fig. S3 (i) FESEM images and (ii) EDX semi-quantitative analysis of elements for (a) C_G , and (b) standard graphite.

Fig. S4 shows N₂ adsorption-desorption isotherms and BJH pore size distribution (inset) of C_G and standard graphite. Both samples illustrated a typical IV isotherm with H3 hysteresis loops that might be characteristic of the mesoporous structure. Accordingly, the samples exhibited a pore size distribution in the mesoporous range of 2-45 nm (inset, Fig. S4). Table S1 shows the BET surface area, pore average diameter, and pore volume results. From Table S1, the surface area and pore volume of the C_G sample is lower than standard graphite. While the pore average diameter is obtained to be higher in C_G as compared to standard graphite. These differences could be attributed to variations in the synthesis process and raw materials used. However, the obtained results are comparable.

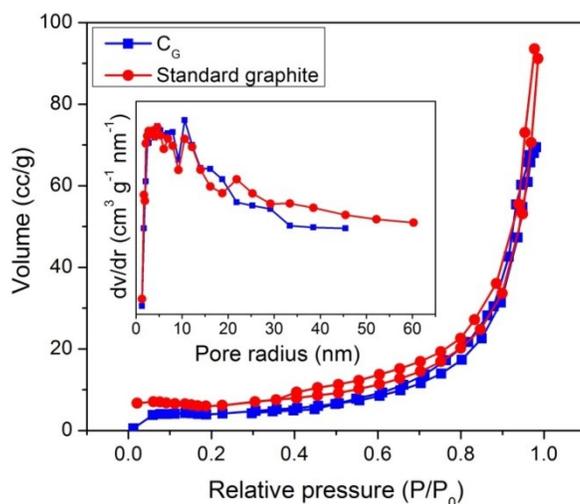


Fig. S4 Adsorption and desorption isotherms and BJH results (inset) for C_G and standard graphite.

Table S1 Results of BET and BJH for C_G and standard graphite.

Sample	C _G	Standard graphite
a _{s, BET} (m ² /g)	14.56	24.45
Pore Average Diameter (nm)	29.51	23.06
V _p (cm ³ /g) (p/p ₀ ≈0.98)	0.11	0.14

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