

Utilization of soybean curd residue for carbon-based adsorbent material and its characterization

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Abstract. Soybean curd residue (SCR) as carbon sources is able for absorbance materials. The utilization of SCR has provided new opportunities and challenges for advanced materials research. The transformation of the carbon structure of the SCR provided graphene-like structures with high surface area and metal ion absorbing capability. The carbon-based adsorbent material was prepared by pyrolysis method. The transformation of carbon structure to produce graphene structure was carried out by Hummers method. Magnetization was carried out by the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to form a magnetite compound (Fe_3O_4) and was applied as absorbance of metal ions. Separation process was carried using magnetic field. The samples were characterized by scanning electron microscopy (SEM), fourier-transform infrared (FTIR), Brauner Emmet Teller (BET) and atomic absorption spectrophotometry (AAS). The results showed that the carbon from the SCR had graphene like-structure which was able to absorb nickel metal ions.

1. Introduction

Fabrication of graphene from natural and industrial waste materials has been carried out by several researchers [1–3]. Various natural wastes have been applied to make graphene such as sugar, jute, rice husk [3], wheat straw [4], wood, leaf, fruit wastes, bagasse, animal wastes and industrial wastes [2]. It shows that graphene can generally be made from high carbon materials such as carbohydrates and proteins. Li *et al* reported that SCR contained carbohydrates in the form of cellulose at about 50 wt% [5].

Graphene is one of carbon structures with many advantages such as high surface area [6], good electrical and thermal conductivity [7], and excellent mechanical flexibility [8]. Graphene can be used as an adsorbent on metal waste. Magnetic material-decorated graphene namely magnetite reduced graphene oxide (MRGO) as adsorbent for metal ion waste has been previously synthesized [9–11]. MRGO is produced to develop the separation process for liquid waste by magnetic separation technique. The process used less energy and was environmentally friendly.

In this research, SCR was used to produce graphene-based structures for MRGO as adsorbent through magnetic separation technique. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) was used to characterize morphology and elemental analysis of MRGO. Fourier-transform infrared (FTIR) was used to analyze chemical structures and the functional groups of graphene and MRGO. Surface area and pore size of graphene were analyzed by Brauner Emmet



Teller (BET) whereas the quantity of metal ion adsorption was carried out by atomic absorption spectrophotometry (AAS).

2. Materials and Method

2.1. Materials and chemicals

Carbon from SCR was processed by pyrolysis at 700 °C for 1 h. This method was adopted from a previous method with minor modification [12]. Graphene was synthesized from carbon-based SCR by Hummers method as described in the previous procedure [2]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were purchased from Sigma-Aldrich to build Fe_3O_4 particle on MRGO. Sulphuric acid, nitric acid, potassium permanganate, hydrochloride acid, hydrogen peroxide, ammonia and ethanol were purchased from Merck Company. Deionized water (DI water) was used for aqueous solutions and rinsing purpose.

2.2. Synthesis of MRGO

MRGO was synthesized by impregnation of Fe_3O_4 particles on graphene as described by previous method [13]. A quantity of 0.3 g of graphene was dissolved in 150 mL DI water and activated using ultrasonic bath for 30 min. Mixture of 25 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution (molar ratio 2:1) was added to graphene under stirring. A 25%wt ammonia solution was added until pH~10 and the temperature was increased up to 80–85 °C for 45 min. The mixture was filtered and washed with ethanol and deionized water several times until neutral condition was achieved. The suspension was oven-dried at 45 °C.



Figure 1. A schematic diagram of MRGO synthesis.

2.3. Application of MRGO in nickel ion waste

MRGO and nickel ion waste solution were mixed with ratio (w/v) of 1:2000. The mixture of MRGO-nickel was shaken for 6 h. Then, MRGO was separated by attaching a magnetic field for 30 min.

2.4. Characterization

The morphology image and elemental identification of the samples were obtained with SEM-EDS (JEOL JSM-IT300) under the operating voltage of 20 kV. The surface area of graphene was measured by BET (Quantachrome NOVA 4200e). FTIR spectra (Nicolet iS5) was recorded to know the functional groups and the existing bonds on MRGO. AAS (SHIMAZU AA6300) were performed to check the quantity of nickel ions.

3. Results and Discussion

Figure 2 illustrates the morphology and elemental analysis of MRGO using SEM-EDS. It shows that the matrix of Fe_3O_4 particle and wrinkle layers could be considered on MRGO surface. The appearance of iron (Fe) element is shown on EDS data. This indicated that Fe particles had been successfully distributed on the surface of MRGO. The EDS data also illustrates other elements such as carbon (C) and oxygen (O). The peak of O element was related to Fe particles from Fe_3O_4 .

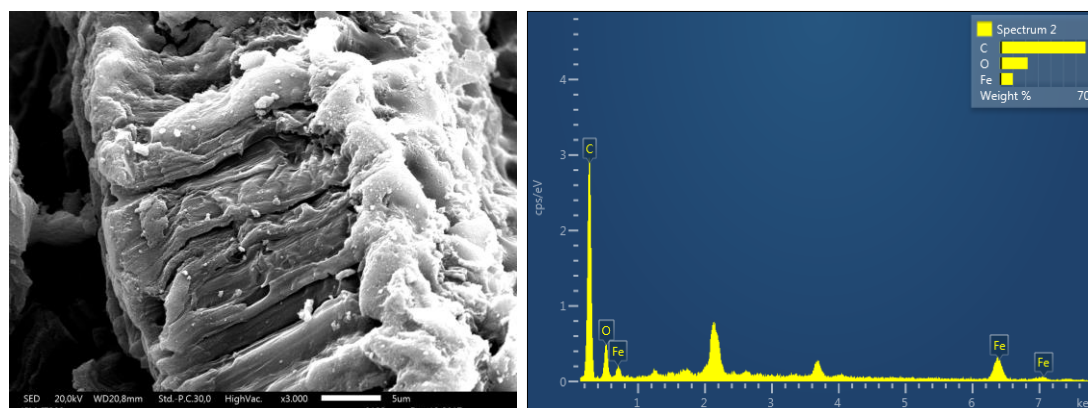


Figure 2. SEM images and EDS data of MRGO.

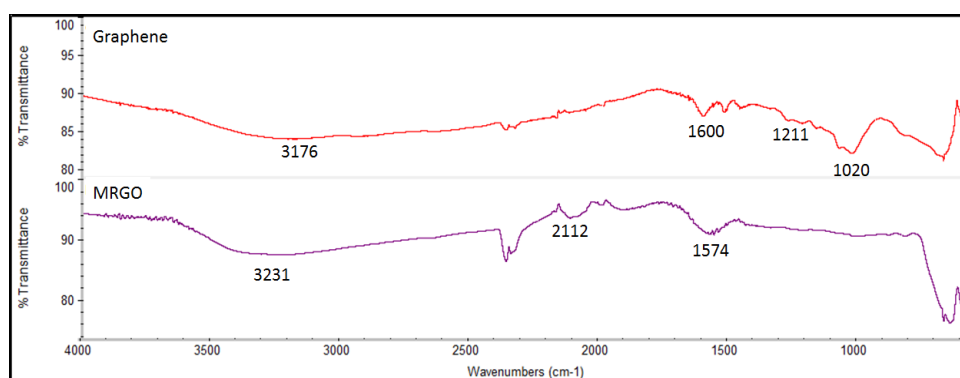


Figure 3. FTIR spectra of graphene and MRGO.

Figure 3 reveals FTIR spectra of graphene and MRGO. FTIR spectra of graphene shows the bands at 1020 cm^{-1} (C=O), 1211 cm^{-1} (C-O), 1600 cm^{-1} (C=C) and 3176 cm^{-1} (O-H). These bands indicated that graphene had been oxidized because the presence of carboxyl, epoxy group, and alkoxy [14]. Then, FTIR spectra of MRGO exhibited the band at 3231 cm^{-1} (O-H) and derivation at the intensity of the adsorption bands of oxygen-containing functional groups [15]. It means that graphene oxide had been reduced on MRGO. Besides, MRGO also showed new bands at 1574 cm^{-1} and 2112 cm^{-1} shows that COO-symmetric vibration was connected with Fe^{3+} [16] and skeletal vibration of graphene sheet [17].

Table 1. BET measurement of graphene.

Surface Area (m^2/g)	Pore Size (nm)	Total Pore Volume (cc/g)
151.472	1.178	0.0892

To determine the surface area and pore size of the graphene, BET measurements were performed. Table 1 shows BET measurements of graphene. Graphene in MRGO had a surface area of $151.472\text{ m}^2/\text{g}$. Based on a reference, graphene oxide had a surface area of $318\text{ m}^2/\text{g}$, represents a decrease in the surface area of the graphene that agglomeration occurred when MRGO was synthesized [11]. In this case, graphene made from carbon-based SCR had a surface area that was not much different with graphene from commercial graphite. Therefore, carbon-based SCR can be an alternative to produce graphene.

To test the absorbance ability, MRGO was applied in nickel metal ion waste. The absorbance result was measured using AAS to determine the alteration of Ni metal ion content in the waste (Table 2).

Table 2. AAS measurements of nickel ion content in waste solution MRGO.

Treatment	Absorbance (a.u)	Ni Content		Ni Adsorbed	
		(ppm)	(%)	(ppm)	(%)
Before	0.0304	77188	100	0	0
After	0.027	67572	87.54	9616	14.23

The result exhibits that there was a reduction of Ni ions before and after treatment. A total of 14% of Ni ion content was absorbed by MRGO. The metal ion adsorption mechanism occurred due to the covalent bonding of the carboxyl group (-COOH) on the graphene surface. The carboxyl group had a negative charge that could bind to nickel ions (Ni^{2+}) [18]. When an external magnetic field was applied, there was an interaction between Ni^{2+} and MRGO. The interaction process of Ni^{2+} that bound to carboxyl group on the graphene surface was subjected to a pull driven by magnetic particles. This caused a decrease of Ni ions content in the solution because it was adsorbed on MRGO. It shows that graphene from SCR can be used as an adsorbent for metal ion waste which have toxic properties. Inexpensive and environmentally friendly materials can be utilized as potential adsorbents for treating water sources contaminated by heavy metals.

4. Conclusion

Utilization of SCR to produce graphene-based structures for MRGO as adsorbent through magnetic separation technique was successfully developed. The metal ions can be decreased as much as 14% in aqueous solution after the application of MRGO and external magnetic field simultaneously.

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