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Fabrication of magnetic carbon composites from peanut shells and its application as a heterogeneous Fenton catalyst in removal of methylene blue

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ABSTRACT

Magnetic carbons were prepared from agricultural waste peanut shells and Ferric ammonium oxalate via a simple impregnation and carbonization process. The obtained composites were characterized by element analysis, MÖssbauer spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, X-ray diffraction, vibrating sample magnetometry and the Brunauer-Emmett-Teller surface area method, respectively. The magnetic carbon material was used as catalyst of heterogeneous Fenton reaction to remove methylene blue with the help of persulfate in waste water. The results indicated that both the removal rate and removal efficiency of this catalytic system are very excellent. The degradation efficiency was best (90% within 30 min) using initial concentrations of 0.5 g L^{-1} persulfate and 40 mg L^{-1} methylene blue. The removal mechanism was investigated by LC-MS. The catalyst retained its activity after seven reuses, indicating its good stability and reusability. It is inexpensive because it consists mainly of agricultural waste. Its porosity contributed to its high activity, which was achieved without any additional activation process. These indicating that the catalyst is potentially useful in the treatment of wastewater.

1. Introduction

An important current environmental research area is the removal of synthetic dyes, which are potential pollutants [1]. Various treatments to decolorize their effluents have been investigated and developed [2]. These include adsorption [3], biological degradation [4], filtration, and advanced oxidation processes [5]. Among these, advanced oxidation processes-which involve various chemical, photo-catalytic, electro-catalytic, or Fenton oxidation methods are attractive, because they can decompose organic pollutants to inorganic and non-toxic compounds such as H_2O, CO_2, and inorganic salts [6–8]. Persulfate ($S_2O_8{}^{2-}$) is an excellent oxidant, which can be effectively activated to generate $SO_4{}^{\bullet-}$ ($E_0 = 2.6$ V) by ultraviolet light, heat or transition metal such as Fe^{2+} and Co^{2+} [9]. Strong oxidizing sulfate free radicals with the advantages of high solubility longer residence time in subsurface than peroxide and wide operative pH range [10]. Persulfate has been successfully used for environmental applications of remediation of dyes, sulfamonomethoxine, tetrabromobisphenol A [11–14].

Magnetic porous carbon composites are of significant interest due to their unique catalytic properties and magnetism. Their composite structures can enhance electron transfer, and they show higher surface areas with more active sites than single magnetic catalysts, leading to their higher activity for the degradation of pollutants in water [15]. Their magnetism enables these catalysts to be easily separated using a magnetic field; they can then be redispersed in solution for reuse. The development of an efficient and inexpensive method for the preparation of useful heterogeneous catalysts is important for the development and application of the Fenton reaction system [16].

The harvesting of crops such as peanuts generates considerable quantities of essentially worthless shells or husks. China, the leading peanut producer worldwide, generates 4.5 million ton of peanut shells annually [17]; the United States, 95.2 thousand metric ton [18]. These vast amounts of peanut shells are currently not greatly valued, but they could be converted into useful and valuable products, such as activated carbon. Several studies have reported the transformation of peanut shells into activated carbon and their subsequent use for absorbing various metal ions and organic

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compounds [19–22]. Most of these transformations require activation processes to form activated carbon with high surface area, which would then be used as an adsorbent. However, physical adsorption cannot thoroughly remove dyes, and the activation processes make the preparation complex and expensive. The development of composites that could be used as catalysts in Fenton-like systems may be more useful [23]. A promising new type of catalyst may be able to combine the advantages of cheap activated carbon and the activity of magnetic particles. The incorporation of magnetic particles inside the pores of the carbon while maintaining its high surface area is the key to the development of such new catalysts.

The present study reports the one-pot synthesis of peanut shell magnetic carbon (PMC) as a catalyst from raw peanut shells and $(NH_4)_3Fe(C_2O_4)_2$, an iron composites precursor. The high-temperature (800 °C) interaction between carbon (from the shells) and iron composites (from the precursors) under a nitrogen atmosphere led to the formation of gases (e.g., H_2O and CO_2) [24], whose subsequent expansion substituted an activation process. Therefore, the preparation became simpler and cheaper. Such a synthesis of magnetic porous carbon composites from agriculture waste for use in Fenton-like reactions has not previously been reported. PMC was then tested as a catalyst in a Fenton-like reaction system, using methylene blue dye (MB) as a substrate. The activity and stability of the PMC were assessed in the adsorption–degradation removal of MB. Their removal mechanism was investigated by LC-MS. PMC was demonstrated to be an excellent catalyst for the removal of MB. Its strong performance combined with its low cost and simple preparation gives the composite great potential practical value.

2. Methods

2.1. Chemicals and materials

Raw peanut shells for the production of magnetic carbon were collected from Shandong, China. $(NH_4)_3Fe(C_2O_4)_3$ was purchased from Shanghai chemical reagent co., LTD.(Shanghai, China), $K_2S_2O_8$ was purchased from Beijing chemical reagent co., LTD. (Beijing, China), $Na_2S_2O_3$ and MB was purchased from Guangfu chemical reagent co., LTD. (Tianjin, China), all chemicals used in this work were of analytical grade and used without further purification. Pristine Fe_3O_4 was prepared with the co-precipitation [25].

2.2. Preparation of PMC

PMC were prepared by impregnation and carbonization processes. The soil-free shells were crushed to reduce the particle size of the catalyst. The properties of the final magnetic carbon produced by chemical impregnation are heavily dependent upon the mass ratio of the materials used [26]. Magnetic precursor ferric ammonium oxalate solutions were prepared to various impregnation ratios defined by the ratio of the dry mass of peanut shell to the mass of $(NH_4)_3Fe(C_2O_4)_3$. Each mixture was dried in an electric oven at 70 °C before heating. The cylindrical precursors were then placed in a tube furnace and carbonized under a 100 $cm^3 min^{-1}$ flow of N_2. Heating to 500 °C first at 5 °C min^{-1}, at which temperature the samples were carbonized for 30 min, before further heating at 10 °C min^{-1} to 800 °C under the same nitrogen flow. The samples were then allowed to cool while the nitrogen stream was maintained. A series of peanut shell magnetic carbon (PMC) catalysts resulted. Sample PMC-0 was prepared without the iron precursor. The other samples had mass ratios of peanut shells to $(NH_4)_3Fe(C_2O_4)_3$ of 15.7, 5.1, and 2.7; they were labeled PMC-1, PMC-2, and PMC-3, respectively.

2.3. Characterization of the materials

The morphology of PMC composites was characterized with scanning electron microscope (SEM JSM-6701F). Elemental analysis (Vario EL element analyzer). MÖssbauer spectra (obtained with a $^{57}Co/Rh$ source at liquid N_2 temperature calibrated with α-Fe). X-ray photoemission spectroscopy (XPS) was recorded on a Kratos ASIS-HS X-ray photoelectron spectroscope equipped with a standard and monochromatic source (Al K_α) operated at 150 W (15 kV, 10 mA). The crystal structure of PMC catalysts was monitored by X-Ray Diffraction (XRD, model D-MAX-RB, Riau, Japan). The parameters of the XRD were Cu, K_α and $l = 0.154$ nm. Magnetic properties were characterized by a vibrating sample magnetometer (VSM, LAKESHORE-7304) at room temperature. The N_2 adsorption–desorption isotherm was measured at liquid nitrogen temperature (76 K) using a Micromeritics ASAP 2010 M instrument. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The reactions were also monitored by LC-MS Trap mass spectroscopy (AB 3200-QTRAP), ESI conditions were as follows: dry gas temperature, 553 K; dry gas (N_2) flow rate, 5 L min^{-1}; nebulizer pressure, 10 psi; capillary voltage, 4.5 kV; skimmer voltage, 30 V; capillary exit, 70 V; the target mass set to 300.

2.4. Degradation of MB by PMC/$K_2S_2O_8$

The heterogeneous Fenton-like oxidation of MB was carried out in a cylindrical Pyrex vessel. 60 mg catalyst was added to 10 mL 40 mg L^{-1} MB solutions. Then 10 mL 1 g L^{-1} $K_2S_2O_8$ solution was added to initiate the reaction. The reaction was carried on for 30 min. MB concentration of the solutions was measured from the standard curve obtained at λ_{max} of 664 nm ($R^2 = 0.999$) using a UV1700 visible spectrophotometer, samplings were taken at a given time intervals during the reaction. Firstly, under the same degraded conditions, compare the catalytic efficiency of different kinds of catalysts. Then in order to found the best degradation factors, different factors were investigated, such as pH, the quantity of catalyst, the concentration of oxidant, the concentration of substrate MB. The kinetic of the degradation procedure was performed as follows: at given intervals, 2 mL samples were drawn out and were mixed immediately with 4 mL 0.2 mol L^{-1} $Na_2S_2O_3$ solution, which was a well-known quenching agent for sulfate radicals and hydroxyl radicals and was used to prevent further reaction [13]. Then the mixture full wavelength scans with UV–vis spectroscopy.

For the recycle runs of MB degradation, the used catalyst was collected by a magnet. The recycled catalyst was re-dispersed into a fresh solution of MB, and the MB degradation was re-initiated by adding the same concentration of PMC. This catalyst recycling and the degradation experiment were repeated seven times.

To evaluate the mineralization of the MB, total organic carbon (TOC) was measured, equipped with an automatic sample injector as described previously. Reported TOC values represent the average of at least two measurements.

The concentration of Fe in the solution was determined using an AA240 atomic absorption spectrophotometer.

The organic compounds in reaction solution after the decolonization were examined using liquid chromatography and mass spectrometry (LC-MS).

3. Results and discussion

3.1. Characterization of PMC

3.1.1. Element analysis

Bulk elemental analysis of Fe-C products is presented in Table 1, with carbon and iron contents determined by difference. More iron