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Synthesis of magnetic yolk-shell mesoporous carbon architecture for the effective adsorption of sulfamethazine drug

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ABSTRACT

In this work, Fe_3O_4@C yolk-shell carbon architecture were fabricated in one pot sol-gel process and further examined as adsorbents for the removal of sulfamethazine. To understand yolk-shell structure on the adsorption properties of sulfamethazine, another adsorbent without hollow cavity, i.e., Fe_3O_4@-SiO_2@C carbon material, was also prepared for comparison. The adsorption results showed the yolk-shell carbon materials complied with the pseudo-second order kinetics model. Based on the Langmuir model the yolk shell material possess a Q_{max} of 312 mg g^{-1}, which is higher than that of core-shell materials (236 mg g^{-1}). Due to the magnetic property, the yolk-shell carbon materials can be retrieved facilely from the aqueous media by an external magnet and 89.1% of recovery can be achieved over five adsorption desorption cycles. Possessing high surface area, a well-defined interface of the material and central cavity the as-prepared material has proved to be a potentially eminent adsorbent for the broad scale removal of sulfamethazine from industrial processes.

1. Introduction

Contemporary the elimination and detection of pollutants from waste water have achieved increasing concern due to their potential treats to human health and ecological systems. With an ever increasing concern, the endeavor to meet the needs of the ever growing population sulfamethazine (SMTz) a class of sulfonamides antibiotics has been synthesized. Mostly used for curing and protection of infectious diseases in humans, enhancing digestion and accelerating the growth of farms animal [1–3]. However, they are partly absorbed and metabolized by humans and animals. Eventually it reaches to the environment through feces and urination [4–7]. Consequently, rifely application of SMTz may prompt antibiotic resistant genes which ultimately will affect the ecosystem and human health [8–13]. A number of assays have been practiced to remove antibiotics such as photolysis [14], hydrolysis, and thermolysis [15], advance oxidation processes [16], as well as biological degradation and adsorption etc [17]. Among these processes, adsorption is the aptest, efficient and effective way to remove antibiotics from aquatic systems [18]. Because of their high elimination performance, simple and easy operation procedure and rife availability of different adsorbent materials [19]. A number of adsorbents have been used for the elimination of SMTz such as nitrogen doped titanium dioxide activated carbon composites [20], pristine and hydroxylated multiwalled carbon nanotubes [21], goethite [22], steam-activated invasive plant-derived biochar [23], and Fe_2O_3/mesoporous silica spheres [24], etc. However, their widespread application in water cleaning is limited by unsatisfactory capacity, regeneration, and recyclability.

Mesoporous carbon materials due to the fascinating features like ample surface area, biocompatibility, thermal stability, chemical inertness and electrical conductivity have achieved huge attention from researchers worldwide [25,26]. As a result, these attributes make it a remarkable and highly potential material. It can be utilized for a number of applications like catalyst support, remediation of pollution, storage of energy, as an agent in the drugs delivery and super capacitors. Due to the unique attributes of mesoporous carbons, such materials have been successfully applied in a number of adsorption based application such as phenol and bilirubin etc. But the problem is to recover the spent materials after

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treatment as they are potentially hazardous to the aquatic life and human health [27,28]. The drawback of isolation and separation can be overcome by incorporating magnetic particles into the matrix. Therefore, integrating different functionalities in a single material will not only be economically favorable but also effective for its bulk use in water remediation as such materials can meet the demands of easy accessibility and enhance reusability [29–31].

Yolk-shell materials a new class of core-shell materials with a magnetic core and a hollow space between the core and shell have fascinated researchers since long times ago due to their unique structure, its high surface area, suitable pore size, low density and huge hollow space between the magnetic core and the shell [32]. Yolk-shell materials have been shown to be particular interesting for applications in drug delivery, gas sensing, battery research and catalysis [33–42]. Carbon materials with a hollow morphology and mesoporous carbon shell have elucidated enhance efficiency in a variety of adsorption based application [43–45]. But the enhanced adsorption efficiency offered by the nanocavity reservoir due to the utilization of the in-cavity volume is yet to be evinced. Eventually, so far it has not been reported that the hollow cavity of such like architectures can be used as a storage spot for adsorbate molecules. While there are very few reports that elucidate the benefit of materials possessing cavity over materials that lack the cavity for adsorption-based applications in pore rather than in cavity. The synthesis of the hollow structure with direct in cavity adsorption is expected to play a key role in adsorption-based applications.

Herein, we report the fabrication of yolk-shell carbon architecture utilizing the Stöber method in a one pot by preparing Fe_3O_4@SiO_2@RF (resorcinol formaldehyde) composite. Thereafter, the composite Fe_3O_4@SiO_2@RF was carbonized under nitrogen. Subsequently, the SiO_2 layer between the magnetic core and the carbon shell was removed to obtain the yolk-shell carbon architecture. This method is interesting as it is very simple, easy and eliminates the multistep processes for fabricating yolk-shell architecture. Materials with such like architecture have many advantages over conventional structures as the shell of the material impede the aggregation of the surrounding particles under extremely harsh conditions, have preferably more exposed active sites as it allows enhance interaction of the guest molecules, the hollow space between the core and the shell act as a storage area making it an attractive material for its use in water remediation technologies. Owing to the strong magnetic property it can easily be collected and reused several times.

2. Experiment

2.1. Materials

Ethylene glycol, ferric chloride hexahydrate, trisodium citrate, sodium acetate, sodium hydroxide, tetraethyl orthosilicate, resorcinol, formaldehyde, ammonia and sulfamethazine drug of analytical grade were purchased from Sinopharm Chemical Reagent (Beijing China) and used without any extra purification. During all the experiments de-ionized water obtained from the laboratory purification system was utilized.

2.2. Synthetic protocol of Fe_3O_4 particles

Aggregates of iron oxide were prepared according to the previously reported method in the literature [46]. In detail, 1.350 g of ferric chloride hexahydrate was dissolved in ethylene glycol solution of 40 ml. Subsequently, 0.4 g tri-sodium citrate and sodium acetate were added under vigorous stirring till the solution becomes clear. Thereafter, the mixture solution was kept at 200 °C for 10 h in a Teflon-lined autoclave in a static condition. Then cool down naturally to ambient temperature. The resultant black products were washed sequentially with de-ionized water and ethanol.

2.3. Synthetic protocol of the magnetic core-shell/shell particles (MCSC)

The as-obtained iron oxide was homogeneously dispersed in a mixture of 160 ml ethanol, 40 ml H_2O and 5 ml ammonia for 30 min through ultrasonication. Then the mixture was shinked into 250 ml round bottom flask and 1.5 ml TEOS were injected gently into the solution under stirring and then 0.4 g resorcinol and 1 ml formaldehyde solution was added and remained it stirring for 24 h. Then it was washed sequentially with de-ionized water and ethanol and dried at 105 °C. Thereafter, the resultant materials were calcined in a tubular furnace at 700 °C for 2 h with a heating rate of 5 °C/min under N_2 atmosphere, resulting in the Fe_3O_4@SiO_2@C (MCSC) materials.

2.4. Synthetic protocol of magnetic yolk-shell carbon architecture (MYSC)

0.2 g of the carbonized sample was shinked into 10 ml of 15 wt% NaOH solution, which was stirred for 24 h at 80 °C to remove the SiO_2 shell. After removing the silica shell, MYSC architecture was obtained and washed with distilled water until the pH of the decanted solution was reached neutral and dried under vacuum at 104 °C for further use.

2.5. Characterization

FT-IR spectra were achieved using the KBr pellets technique on an FT-IR spectrometer (American Nicolet Corp. Model 170-SX) in a transmission mode. Nitrogen adsorption-desorption isotherms were collected at 77 K using a Micromeritics 2020 analyzer (USA). TEM (transmission electron microscopy) analysis was conducted on a TECNAI G2 20 LaB6 electron microscope operated at 200 kV. SEM (scanning electron microscopy) analysis was conducted on an FEI Quanta 250F system. XRD patterns were recorded on a Bruker AXS D8 advance powder diffraction system using Cu Kα($\lambda = 1.5418$ Å) radiation. The magnetic properties of the samples were measured by the vibrating sample magnetometer (Lakeshore 7400Series) in the applied field sweeping from −10000 to 10000 O_e. The XPS spectra were obtained by using a PHI Quantera II ESCA System with Al Kα radiation at 1486.8 V.

2.6. Adsorption experimental procedures

In a typical procedure, 10 mg materials were dispersed in a 30 ml 100 ppm SMTz solution at pH = 6 in glass bottles placed in shaker orbital at temperature 25°C and 180 rpm. NaCl solution was used to adjust the ionic strength to 10 mmol l^{-1}. Successively at a specific time interval, 1 ml solution was extracted through a syringe and the supernatant was obtained by filtration using 0.45 μm Millipore membrane. The residual concentration of SMTz was acknowledged at wavelength 263 nm by PerkinElmer UV-Spectrophotometer Lambda 750.

A kinetic study was managed to evaluate the time of equilibrium for SMTz adsorption by MYSC and MCSC at a 100 ppm concentration of SMTz and stirred for different time intervals (5–360 min). A control test was conducted (between iron oxide and SMTs) to better understand the adsorption mechanism. Adsorption isotherm studies were managed at a concentration ranging from 20 to 160 ppm SMTz at pH = 6. After a contact time of 360 min, samples were extracted as the same way discussed above.