

Magnetically Modified Coffee Silverskin for the Removal of Xenobiotics from Wastewater

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Coffee silverskin (CS), a solid waste from the coffee industry, was magnetically modified by contact with an aqueous ferrofluid containing magnetite nanoparticles. The resulting material was characterized by SEM-EDX analysis and X-ray diffraction.

To assess the suitability of the magnetically modified CS for the removal of pollutants from wastewaters, both equilibrium and kinetic adsorption experiments were performed. Methylene blue was used as a model contaminant. Equilibrium and kinetic data were fitted by the Langmuir equation and the pseudo-second-order model. A maximum adsorption capacity of 556 mg g⁻¹ and a half-adsorption time ranging from 12.8 to 35.3 min were determined. The magnetically modified adsorbent was regenerated by washing with 0.01 N HCl and recovered from the aqueous solution by a permanent magnet.

Overall, the results obtained strongly support the use of the magnetic material developed as a new low-cost adsorbent for the large-scale removal of pollutants from wastewater.

1. Introduction

Adsorption is one of the most effective physical processes for the removal of pollutants from wastewater (Dabrowski, 2001). Most commercial systems currently use activated carbon as the adsorbent because of its excellent adsorption capacity and versatility. However, the high costs of manufacturing and regeneration make activated carbon an expensive material (San et al., 2001). For these reasons, many approaches have been attempted, in recent years, to produce low-cost alternatives to activated carbon (Gupta et al., 2009). A low-cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little or no processing (Aksu and İšoğlu, 2005). Bentonite, kaolinite, zeolites, silica beads, industrial by-products, plant and agricultural wastes are just some examples of the materials that are potentially suitable for this purpose (Gupta et al., 2009).

Agricultural wastes are available in large quantities worldwide and their use as adsorbents (Lavecchia et al., 2010) or for other applications such as the recovery of antioxidant compounds (Panusa et al., 2013) or the production of energy (Zuorro and Lavecchia, 2011) could greatly contribute to reducing the disposal costs and their impact on the environment.

Coffee silverskin (CS) is a by-product of the coffee roasting process and consists of the innermost skin of the coffee bean. During roasting, a variety of chemical and structural changes occur which lead to the separation of this tegument from the beans. CS has no commercial value and is currently disposed of as a solid waste or simply burned. Despite its structural and compositional similarities to other lignocellulosic materials (Borrelli et al., 2004), no study has so far been made to evaluate its potential as a low-cost adsorbent. One reason is to be found in the fact that CS is produced in the form of a very light ash-like material, which makes its use in both laboratory and large-scale operations quite problematic.

In this contribution we have investigated the possibility of magnetizing CS by contacting the material with a ferrofluid containing magnetite nanoparticles. As demonstrated by studies on other magnetically modified adsorbents, such as spruce sawdust (Safarik et al., 2007), black tea leaves (Safarik et al., 2012a) and spent coffee grounds (Safarik et al., 2012b), magnetization allows easy manipulation and recovery by an external magnetic field. This suggests that they could be advantageously used for large-scale removal of contaminants from polluted water sources. In order to assess the suitability of the magnetically modified

CS for such applications, we performed a preliminary study using methylene blue, a cationic phenothiazine dye, as model contaminant.

2. Experimental

2.1 Materials

CS was obtained from a local coffee roaster. Ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), tetramethylammonium hydroxide (TMAH, 25 wt.% in water), hydrogen chloride, sodium hydroxide, ethyl alcohol and methylene blue were purchased from Sigma (Milano, Italy). All other chemicals were of analytical grade and used without further purification.

Methylene blue solutions were prepared by dissolving appropriate amounts of the dye in distilled water.

2.2 Preparation of adsorbent

In order to remove soluble and coloured compounds, CS was washed several times with hot water until the washing solution was colorless. The solid was then rinsed and oven dried at $50\text{ }^\circ\text{C}$ for 24 h. Finally, CS was ground, sieved to $<500\text{ }\mu\text{m}$ and stored at room temperature in the dark until use.

2.3 Magnetic modification of CS

Aqueous ferrofluid was prepared according to the procedure reported by Berger et al. (1999) with some modifications. Briefly, magnetite (Fe_3O_4) nanoparticles were first produced by combining FeCl_3 and FeCl_2 in a 2:1 stoichiometric ratio in aqueous 1 M ammonia solution. The precipitate was recovered and treated with TMAH solution. Then, the crystallites were magnetically decanted and washed several times with distilled water to remove water-soluble impurities. Finally, the solid was resuspended in distilled water.

For preparation of the magnetically modified material, 3.75 g of CS were suspended in 30 mL ethanol with 3 mL of ferrofluid. The suspension was stirred for 1 h at room temperature. Then, the magnetically modified CS was repeatedly washed with ethanol and air dried.

2.4 Characterization of magnetically modified CS

The morphological analysis of CS samples was carried out by a scanning electron microscope (SEM S-2500, Hitachi, Japan) equipped with an EDX analyser. X-ray diffraction (XRD) analysis was performed with a Philips X'Pert PRO diffractometer (Philips, The Netherlands) using $\text{Cu K}\alpha$ radiation at $\lambda = 1.5418\text{ \AA}$. Diffraction patterns were recorded from 5° to $60^\circ 2\theta$ at a scan rate of 1° min^{-1} .

2.5 Adsorption studies

Adsorption experiments were performed in batch mode as described elsewhere (Zuorro et al., 2013). Briefly, CS and the dye solution were initially loaded into glass flasks, which were stirred at room temperature ($20 \pm 2\text{ }^\circ\text{C}$) for the required time. Then, the adsorbent was separated from the suspension using a permanent magnet and the clear solution was analysed for dye content (Zuorro and Lavecchia, 2013). The concentration of methylene blue was determined spectrophotometrically at 665 nm, where the absorption spectrum of the dye displays a maximum (Figure 1). At this wavelength, a molar extinction coefficient of $4.73 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$ was obtained from standard solutions of methylene blue in water

Regeneration of the adsorbent was accomplished by treating the dye-loaded material with 0.01 N aqueous HCl (5-min contact at room temperature, with a liquid-to-solid ratio of 2 mL mg^{-1}).

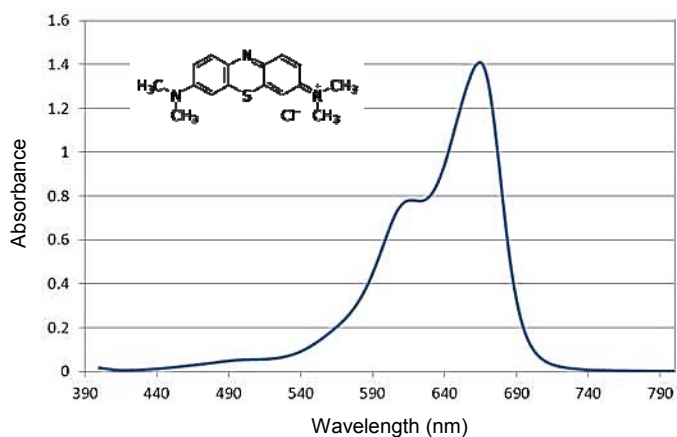


Figure 1: Absorption spectrum of methylene blue

3. Results and discussion

3.1 Characterization of magnetically modified CS

Figure 2 shows a SEM image of CS. As can be seen, the material exhibits a highly corrugated surface structure with an entangled network of fibers. No differences in surface morphology were observed between untreated and magnetically modified CS. EDX analysis revealed the presence of C and O, S, Ca, K as major elements, in addition to Fe for the magnetic samples.

The XRD pattern of magnetically modified CS is presented in Figure 3. The six characteristic peaks at $2\theta = 29.9^\circ, 35.3^\circ, 42.8^\circ, 53.2^\circ$ and 56.9° correspond to the planes (220), (311), (400), (422) and (511) of magnetite (Fe_3O_4). This indicates that, upon exposure of CS to the water-based ferrofluid, magnetite nanoparticles or their aggregates are deposited on the surface of CS, thereby resulting in the formation of the magnetic adsorbent.

The average size of magnetite crystallites was estimated from the strongest diffraction peak (311) by the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where D is the average crystallite size, λ is the wavelength of Cu $K\alpha$ radiation, β is the full-width at half maximum of the peak and θ is the Bragg diffraction angle. We obtained $D = 10.4$ nm.

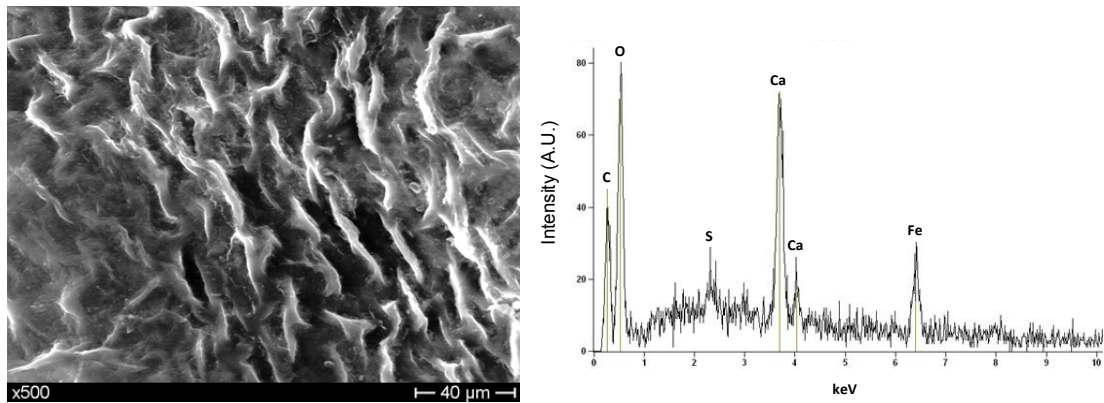


Figure 2: SEM image and EDX spectrum of magnetically modified CS

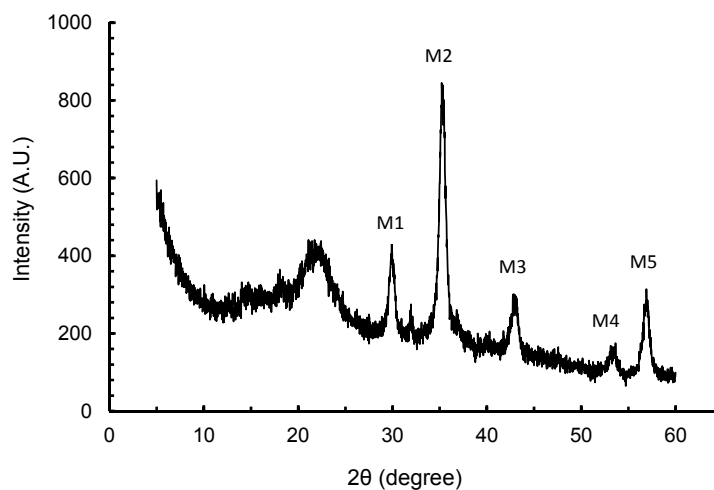


Figure 3: XRD pattern of magnetically modified CS with the characteristic peaks of magnetite (M1 to M5)

3.2 Adsorption studies

These studies were performed to evaluate the potential of CS for the removal of methylene blue from aqueous solution. Preliminary experiments showed no appreciable differences between the untreated and the magnetically modified CS, suggesting that the magnetite particles and/or the magnetization procedure did not affect the adsorption capacity of the material. The same conclusion was reached in studies on the magnetization of similar plant-based materials, such as tea leaves (Safarik et al., 2012a) and spent coffee grounds (Safarik et al., 2012b).

Equilibrium adsorption experiments were conducted at room temperature and pH around 6 by contacting 50 mg of CS with 100 mL of the dye solution. The initial dye concentration was varied between 25 and 1,000 mg L⁻¹. Under these conditions, the adsorption of methylene blue reached equilibrium in approximately 2 h. Hence, a contact time of 3 h was selected for subsequent testing.

The equilibrium data were analysed by the Langmuir and the Freundlich models:

$$q^* = \frac{q_{max} K_L c^*}{1 + K_L c^*} \quad (2)$$

$$q^* = K_F c^{*n} \quad (3)$$

where c^* and q^* are the equilibrium concentrations in the liquid and solid phases, q_{max} is the maximum adsorption capacity, K_L is the Langmuir equilibrium constant, and K_F and n are the Freundlich constants.

As can be seen from Figure 4, the Langmuir model provided a more accurate description of the adsorption process. The estimated Langmuir parameters were: $q_{max} = 556 \text{ mg g}^{-1}$ and $K_L = 1.03 \times 10^{-4} \text{ mM}$.

An examination of the literature reveals that the adsorption capacity of CS for methylene blue was very close to that of papaya seeds (Hameed, 2009) but significantly higher than those of other low-cost adsorbents, which were roughly between 10 and 350 mg g⁻¹ (Bhatnagar and Sillanpää, 2010). Interestingly, it was also higher than those of activated carbons produced from waste biomass such as bamboo (Hameed et al., 2007) and oil palm fibre (Tan et al., 2007).

The very high adsorption capacity of CS for methylene blue may be due to the favourable electrostatic interactions between the positively charged dye molecule and the oppositely charged adsorbent surface. It is known, in fact, that lignocellulosic plant materials like CS contain many negatively charged surface sites, such as the hydroxyl and carboxyl groups on the cellulose fibers and those in proteins and phenolic compounds (Demirbas, 2008). Furthermore, high levels of melanoidins are also found in CS (Borrelli et al., 2004). These compounds are formed during coffee roasting through the Maillard reaction. As demonstrated by recent studies, coffee melanoidins are negatively charged molecules due to the presence of uronic acids and other unidentified components (Bekedam et al., 2007).

The kinetics of dye adsorption was studied by contacting 50 mg of CS with 100 mL of the dye solution at room temperature and pH around 6. The initial dye concentration was set at 50, 100 and 300 mg L⁻¹, and the dye concentration in the aqueous solution was monitored for up to 6 h.

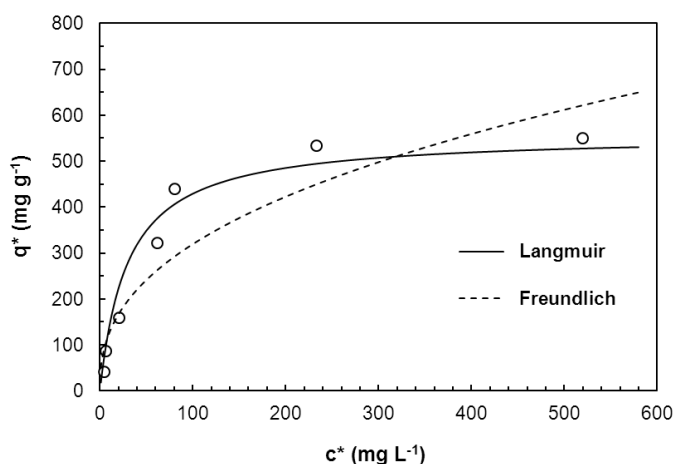


Figure 4: Adsorption equilibrium data of methylene blue on magnetically modified CS

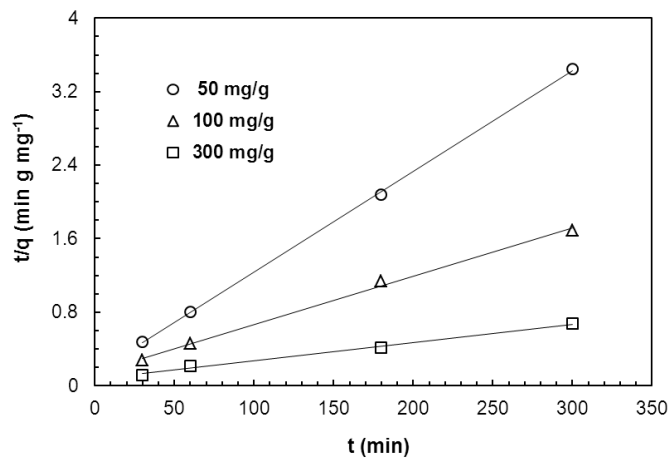


Figure 5: Pseudo-second-order model for the adsorption of methylene blue on magnetically modified CS

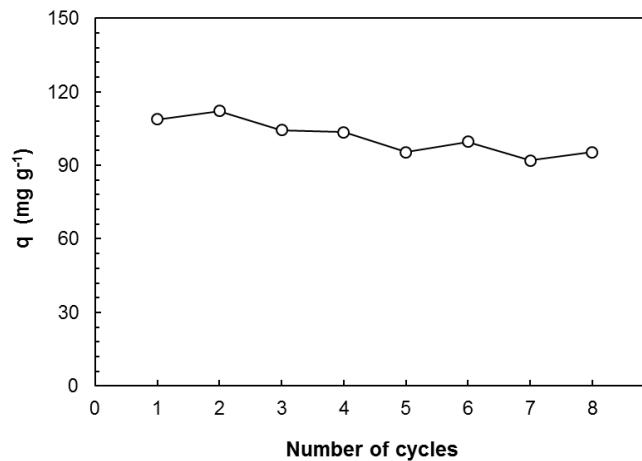


Figure 6: Amount of methylene blue adsorbed per unit weight of magnetically modified CS after each cycle of regeneration

Several kinetic models, including the pseudo-first-order model, the pseudo-second-order model and the Elovich model, were used to analyse the kinetic data. The pseudo-second-order model provided the best correlation. The linearized form of this model is given by (Ho and McKey, 1998):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q is the amount of solute adsorbed per unit weight of solid at time t , and k_2 and q_e are model parameters to be estimated from the data. Figure 5 shows the good agreement between experimental and calculated results ($R^2 > 0.993$). From the k_2 and q_e values, the half-adsorption time can be easily calculated as (Doğan et al., 2009):

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (5)$$

The quantity $t_{1/2}$ represents the time required for the adsorbent to uptake half of the maximal amount of solute and therefore provides a quantitative measure of the adsorption rate. By substituting the k_2 and q_e values in eq. (5), a half-time ranging from 12.8 to 35.3 min was obtained.

3.3 Regeneration of the adsorbent

The possibility of regenerating the magnetically modified adsorbent for reuse purposes was investigated by conducting multiple adsorption/desorption cycles. Under the conditions tested, the adsorbent regeneration was very fast and effective. As is evident from Figure 6, the adsorption capacity of CS was only slightly affected by the regeneration procedure for at least eight cycles. This adds further value to the use of magnetically modified CS in industrial applications.

4. Conclusions

The results of this study clearly demonstrate that CS, a waste material from the coffee industry, can be easily transformed into a low-cost magnetic adsorbent by a ferrofluid treatment. The magnetically modified CS acted as an effective adsorbent for the removal of methylene blue, a cationic phenothiazine dye, from aqueous solution and was easily regenerated. These properties make the magnetic material developed highly suitable as a new low-cost adsorbent for the large-scale removal of pollutants from wastewaters.

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