CHEMICAL ENGINEERING TRANSACTIONS
VOL. 38, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Enrico Bardone, Marco Bravi, Taj Keshavarz

ISBN 978-88-95608-29-7; **ISSN** 2283-9216
DOI: 10.3303/CET1438059

Magnetically Modified Agro-Industrial Wastes as Efficient and Easily Recoverable Adsorbents for Water Treatment

Antonio Zuorro*, Roberto Lavecchia, Stefano Natali

Dipartimento di Ingegneria Chimica, Materiali e Ambiente, Sapienza University, Via Eudossiana 18, 00184 Roma, Italy
antonio.zuorro@uniroma1.it

Defective green coffee (DGC), coffee silverskin (CS) and spent coffee grounds (SCG), three major by-products of the coffee industry, were magnetically modified by treatment with an aqueous ferrofluid containing magnetite nanoparticles and characterized by SEM, XRD and FTIR. In order to assess their suitability as adsorbents for the removal of pollutants from wastewaters, adsorption and regeneration studies were carried out using methylene blue as a model contaminant. All the materials exhibited high adsorption capacity and the adsorption rate varied in the order: CS > SCG > DGC. In addition, their adsorption capacity remained almost unchanged for at least six adsorption/desorption cycles. These results strongly support their use as new low-cost adsorbents for environmental applications.

1. Introduction

Because of its efficiency, versatility and ease of operation, adsorption is one of the most common methods for the removal of pollutants from industrial effluents. An ideal adsorbent should have high adsorption capacity, good selectivity and easy regenerability. Among adsorbents, activated carbon seems to offer the best compromise on overall performance and is therefore the most widely used material. However, it is quite expensive and its regeneration cost is also high. For these reasons, there is currently great interest in finding low-cost alternatives to activated carbon (Ali et al., 2012).
A low-cost adsorbent can be defined as one that is abundant in nature, or is a by-product or waste from industry, and requires little or no processing (Aksu and İşoğlu, 2005). Zeolites, clay materials, microbial biomass, industrial by-products and agricultural wastes are some of the materials that have been proposed and tested to date (Gupta et al., 2009). Besides being inexpensive, agricultural and agro-industrial wastes are renewable and widely available in nearly all parts of the world. Furthermore, their use as adsorbents could contribute to reducing both the disposal costs and their impact on the environment.
As attested by the over 7 million tons of green coffee beans produced each year (ICO, 2012), coffee is one of the most popular and consumed beverages in the world. From the processing of coffee fruits to the production of coffee beverages or instant coffee, huge amounts of by-products and wastes are generated. They include coffee husks, parchment, defective coffee beans, coffee silverskin and spent coffee grounds.
In this study we focused on the three major by-products of the coffee industry: defective green coffee (DGC), coffee silverskin (CS) and spent coffee grounds (SCG). DGC, also known as low-grade green coffee, represents about 15–20% by weight of the total production. Although sometimes blended with the non-defective one, DGC is usually disposed of as a waste product due to the undesirable taste imparted to the coffee beverage. Coffee silverskin (CS), a by-product of the coffee roasting process, consists of the innermost skin of the coffee bean (Murthy and Naidu, 2012). During roasting, this tegument undergoes chemical and structural changes which lead to its fragmentation and separation from the beans. SCG is the solid residue from the production of coffee beverages or the manufacturing of instant coffee (Panusa et al., 2013). Studies over the last few years have shown that these materials could be used as low-cost adsorbents for the removal of pollutants from wastewater. For example, untreated coffee grounds were found to exhibit good adsorption properties towards cadmium (Azouaou et al., 2010) and lead (Lavecchia et al., 2010). Similarly, degreased green coffee beans were used as effective adsorbents for the removal of malachite green from aqueous solution (Baek et al., 2010).

Please cite this article as: Zuorro A., Lavecchia R., Natali S., 2014, Magnetically modified agro-industrial wastes as efficient and easily recoverable adsorbents for water treatment, Chemical Engineering Transactions, 38, 349-354 DOI: 10.3303/CET1438059

The main aim of our research was to investigate the possibility of magnetizing DGC, CS and SCG so as to produce adsorbents that can be easily handled and recovered from the treated solution by an external magnetic field. To this end, the three materials were contacted with a ferrofluid containing magnetite nanoparticles and the resulting magnetically modified adsorbents characterized by SEM, XRD and FTIR. In order to test the adsorption properties of these materials, the cationic phenothiazine dye methylene blue was used as a model contaminant.

2. Experimental

2.1 Materials

DGC and CS were obtained from local producers in Brazil and Italy, respectively. SCG were from a coffee bar in Rome (Italy).

Ferrous chloride ($FeCl_2$•$4H_2O$), ferric chloride ($FeCl_3$•$6H_2O$), tetramethylammonium hydroxide ($C_4H_{13}NO$, 25 wt% in water), ammonia, hydrogen chloride, sodium hydroxide, ethyl alcohol and methylene blue ($C_{16}H_{18}N_3SCl$) were purchased from Sigma (Milano, Italy). All chemicals were of analytical grade and used without further purification.

2.2 Preparation of magnetic adsorbents

In order to remove soluble and coloured compounds, the three wastes were washed several times with hot water, left to dry in air for 8 h and then oven-dried at 50 °C for 24 h. DGCB were ground in an electric coffee grinder and sieved to <500 μm. Moisture content was measured by an electronic moisture analyzer (MAC 50/1, Radwag, Poland).

An aqueous ferrofluid was prepared as described elsewhere (Zuorro et al., 2013). Briefly, magnetite (Fe_3O_4) nanoparticles were first produced by combining $FeCl_3$ and $FeCl_2$ (in a 2:1 stoichiometric ratio) in 1 M ammonia solution. The precipitate was recovered and treated with the tetramethylammonium hydroxide solution. Then, the resulting crystallites were magnetically decanted and washed several times with distilled water. Finally, the solid was resuspended in distilled water and stored at 4 °C.

The magnetic adsorbents were prepared by suspending 5 g of the solid in 40 mL ethanol and 5 mL ferrofluid. The suspension was stirred for 1 h at room temperature. After this time, the solid was recovered by a permanent magnet, washed repeatedly with ethanol and air dried.

2.3 Characterization of magnetic adsorbents

Morphological analysis of the materials was performed by a scanning electron microscope (SEM S-2500, Hitachi, Japan) equipped with an EDX analyser.

X-ray diffraction (XRD) measurements were carried out on a Philips X'Pert PRO diffractometer (Philips, The Netherlands) with a monochromatic Cu Kα radiation (λ = 0.15405 nm) at 1.6 kW (40 kV, 40 mA). Diffraction patterns were recorded in a step-scan mode between 5° and 120° 2θ values, with a step size of 0.02° and a counting time of 4 s per step.

FTIR spectra were acquired in the mid-IR region (4000–400 cm^{-1}) using a Bruker Vertex 70 spectrometer equipped with a Platinum ATR sampling module.

2.4 Adsorption and regeneration studies

The adsorbate solution was prepared by dissolving methylene blue in distilled water. Batch adsorption experiments were performed in magnetically stirred flasks at room temperature (20 ± 2 °C) and pH 5.5 ± 0.1. In a typical run, 0.05 g of the magnetic biosorbent and 100 mL of the dye solution were loaded into the flasks and stirred for the required time. Then, a permanent magnet was placed at the bottom of the flask, the adsorbent separated from the liquid and the solution assayed for dye content. Measurements were performed by a double-beam UV-Vis spectrophotometer (Lambda 25, Perkin Elmer, USA) against a blank of distilled water. Methylene blue concentration was determined from the absorbance at 665 nm, where the dye spectrum has a maximum, using a molar extinction coefficient of 4.73×10^3 M^{-1} cm^{-1}.

Regeneration tests were carried out at room temperature by treating the dye-loaded adsorbent with 0.01 N aqueous HCl. In most experiments, the liquid-to-solid ratio was set to 2 L g^{-1} and the contact time was varied between 5 and 20 min.

3. Results and discussion

3.1 Characterization of magnetic adsorbents

Figure 1 shows SEM images of the three magnetically modified adsorbents. DGC and SCG exhibited similar morphological features, with a highly porous and irregular structure. CS was characterized by a three-dimensional network of fibers aligned in some preferred orientation. No apparent differences were

observed between the magnetized and non-magnetized materials. EDX analysis revealed that C, O, S, Ca and K (plus Fe, in magnetized samples) were the major elements present.

XRD patterns of the magnetic adsorbents are presented in Figure 2. The diffractograms of the three materials were very similar and characterized by the presence of a number of well-defined Bragg peaks in the 2θ region between 20° and 80°. The most prominent peaks corresponded to reflections from the planes (211), (220), (311), (400), (422), (511), (440) and (533) of magnetite.

The average crystallite size of magnetite was estimated from the strongest diffraction peak (2θ = 35.5°) using the Debye-Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

where D is the crystallite size, λ is the incident X-ray wavelength, β is the full width at half-maximum height and θ is the Bragg angle.

An approximate evaluation of the surface area of magnetite was made by assuming it to consist of spherical particles of the same size and density, which yields:

$$S = \frac{6000}{\rho D} \tag{2}$$

where S is the surface area ($m^2\ g^{-1}$) of magnetite, ρ is its density (5.18 g cm^{-3}) and D is the crystallite size (nm). The results are summarized in Table 1. As can be seen, S ranged from about 82 to 95 $m^2\ g^{-1}$ and D was between 12.2 and 14.2 nm.

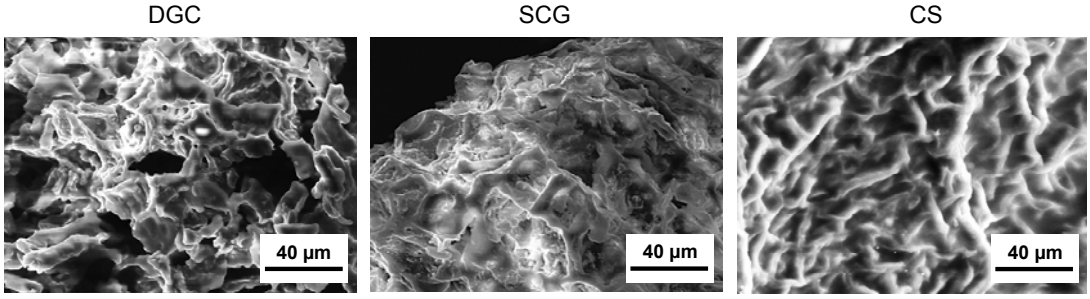

Figure 1: SEM images of green coffee (DGC), spent coffee grounds (SCG) and coffee silverskin (CS)

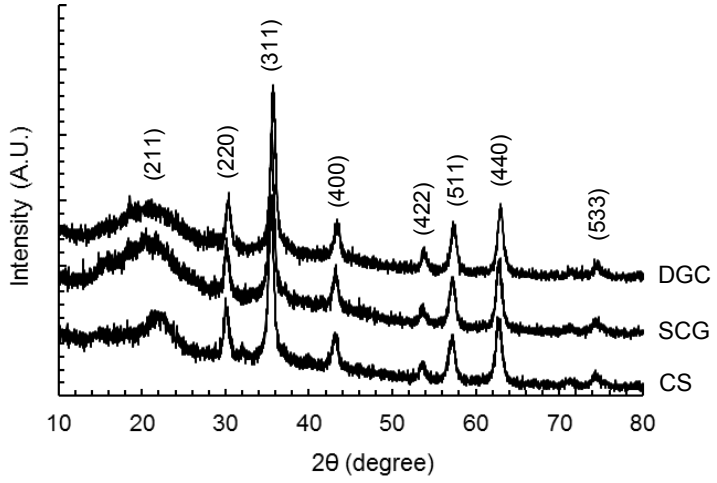

Figure 2: XRD patterns of green coffee (DGC), spent coffee grounds (SCG) and coffee silverskin (CS)

Table 1: Average crystallite size (D) and surface area (S) of magnetite nanoparticles determined from XRD data

Material	D (nm)	S (m^2 g^{-1})
DGC	12.8	90.49
SCG	14.2	81.57
CS	12.2	94.94

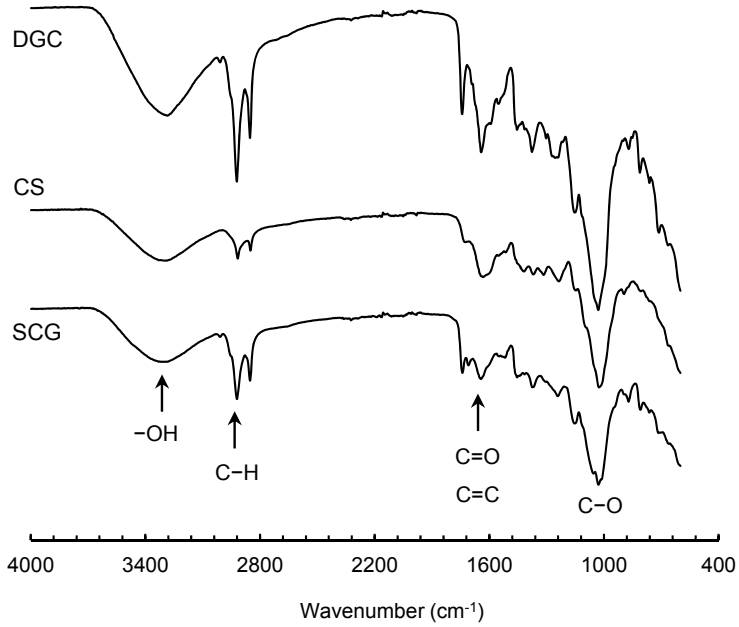

Figure 3: FTIR spectra of green coffee (DGC), coffee silverskin (CS) and spent coffee grounds (SCG)

FTIR spectra showed the presence of a number of characteristic peaks (Figure 3), which were attributed to the stretching vibrations of OH groups (3300 cm^{-1}), aliphatic CH groups (2950–2900 cm^{-1}), C=O or C=C groups (1640–1650 cm^{-1}) and carbonyl groups (1020–1030 cm^{-1}). The presence of these peaks in FTIR spectra can be easily explained by considering the structural features of the three waste materials which contained cellulose, hemicellulose and lignin as main components.

Based on the results of the characterization of the three materials, we can therefore conclude that magnetite nanoparticles or their aggregates are deposited on the surface of DGC, CS and SCG as a result of the treatment with the aqueous ferrofluid and that this procedure does not affect the structural properties of the adsorbents.

3.2 Adsorption and regeneration studies

These experiments were conducted to investigate the adsorption properties of the three waste materials and highlight possible changes in their adsorption behaviour induced by the magnetization procedure. As already said, methylene blue was used as a model contaminant.

The amount of adsorbed dye, q (mg g^{-1}), calculated as:

$$q = \frac{V_L}{m}(c_0 - c) \tag{3}$$

where c_0 and c are the initial and final dye concentrations (mg L^{-1}) in the liquid, V_L is the solution volume (L) and m is the dry mass of adsorbent (g).

Several kinetic models, including the pseudo-first-order model, the Elovich model and the pseudo-second-order model, were used to describe the variation of q with time. The pseudo-second-order model provided the best fit to observations. Accordingly, the following differential equation was used to model the adsorption data (Wu et al, 2009):

$$\frac{dq}{dt} = k(q_e - q)^2 \tag{4}$$

where k (g mg^{-1} min^{-1}) is the rate constant of adsorption, q (mg g^{-1}) is the amount of solute adsorbed per unit weight of solid at time t and q_e (mg g^{-1}) is the value of q at equilibrium.
Integration of the above equation with the initial condition q(0) = 0 and rearrangement yields:

$$\frac{t}{q} = \frac{1}{kq_e^2} + \frac{t}{q_e} \tag{5}$$

that is, a linear dependence of t/q on t.
As is evident from Figure 4, where some representative results are shown, the agreement between experimental and calculated results was very good. The parameters k and q_e were estimated by least-squares regression analysis, which gave the results reported in Table 2. In the same table, the values of the initial adsorption rate (r_0) and the half-adsorption time ($t_{1/2}$) for the three materials are also presented. r_0 is the rate of dye adsorption at t = 0 while $t_{1/2}$ is the time required for the adsorbent to uptake half of the maximal amount of solute. Both parameters therefore provide a measure of the adsorption rate. They were calculated as:

$$r_0 = kq_e^2 \tag{6}$$

$$t_{1/2} = \frac{1}{kq_e} \tag{7}$$

From Table 2 it can be seen that all the materials exhibited high adsorption capacity, their q_e value ranging from 66.2 to 99 mg g^{-1}. This may be mostly due to favorable electrostatic interactions between the positively charged dye molecules and the oppositely charged adsorbent surface. It is known, in fact, that lignocellulosic materials like coffee silverskin and coffee beans contain many negatively charged surface sites, such as the hydroxyl and carboxyl groups of cellulose and others found in proteins and phenolic compounds (Demirbas, 2008). The presence of high levels of negatively charged melanoidins (Moreira et al., 2012) in roasted coffee beans and, particularly, coffee silverskin, is perhaps responsible for the higher adsorption capacity of CS and SCG compared to DGC. The adsorption rate, as deduced from the values of r_0 and $t_{1/2}$, varied in the order: CS > SCG > DGC.
Finally, regeneration tests carried out by repeated adsorption/desorption cycles showed that the adsorption capacity of the three materials remained almost unchanged (observed variations < 7%) for at least six cycles.

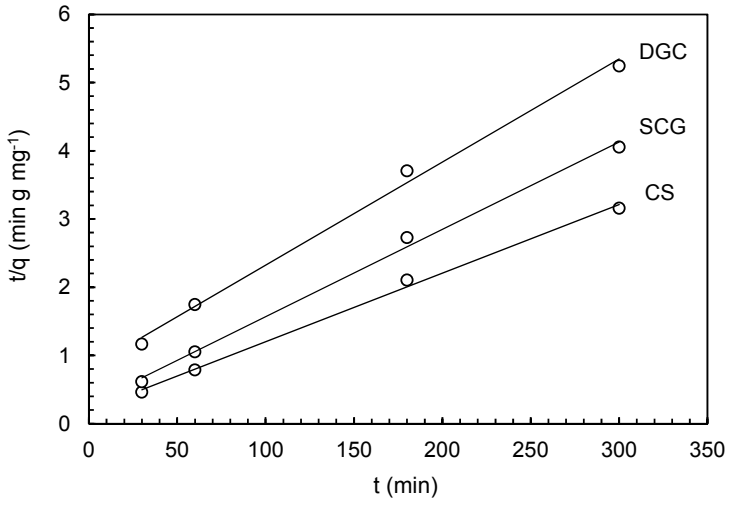

Figure 4: Kinetics of dye adsorption on the three materials (m = 0.05 g, V_L = 0.1 L, c_0 = 50 mg L^{-1})

Table 2: Adsorption kinetic parameters for the pseudo-second-order model

Material	k (g mg^{-1} min^{-1})	q_e (mg g^{-1})	r_0 (mg g^{-1} min^{-1})	$t_{1/2}$ (min)
DGC	2.81×10^{-4}	66.2	1.23	53.74
CS	5.28×10^{-4}	99.0	5.17	19.14
SCG	5.69×10^{-4}	78.1	3.48	22.48

4. Conclusions

The results of this study demonstrate that DGC, CS and SCG, three major by-products of the coffee industry, can be easily transformed into low-cost magnetic adsorbents by a ferrofluid treatment. The magnetically modified materials acted as effective adsorbents for the removal of the cationic dye methylene blue from aqueous solution. In addition, they were easily recovered from the solution by a permanent magnet and readily regenerated by washing with aqueous hydrochloric acid. Although further research is needed to assess their suitability for industrial applications, the present results clearly support their potential as new low-cost adsorbents for the removal of pollutants from wastewaters.

Acknowledgements

The authors gratefully thank Prof. Maria Laura Santarelli for her assistance in FTIR measurements and valuable discussion.

References

Aksu Z., İşoğlu I.A., 2005, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem., 40, 3031–3044.

Ali I., Asim M., Khan T.A., 2012, Low cost adsorbents for the removal of organic pollutants from wastewater, J Environ. Manage., 113, 170 –183.

Azouaou N., Sadaoui Z., Djaafri A., Mokaddem H., 2010, Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics, J. Hazard. Mat., 184, 126–134.

Baek M.H., Ijagbemi C.O, Se-Jin O., Kim D.S., 2010, Removal of malachite green from aqueous solution using degreased coffee bean, J. Hazard. Mat., 176, 820–828.

Demirbas A., 2008, Heavy metal adsorption onto agro-based waste materials: A review, J. Hazard. Mater., 157, 220–229.

Gupta V.K., Carrott P.J.M., Ribeiro Carrott M.M.L., Suhas, 2009, Low-cost adsorbents: growing approach to wastewater treatment – A review, Crit. Rev. Env. Sci Technol, 39, 783–842.

ICO, International Coffee Organization, 2012, Total Coffee Production of Exporting Countries, London (UK), <www.ico.org/trade_statistics.asp> accessed 10.12.2013.

Lavecchia R., Pugliese A., Zuorro A., 2010, Removal of lead from aqueous solutions by spent tea leaves, Chemical Engineering Transactions, 19, 73–78.

Moreira A.S., Nunes F.M., Domingues M.R., Coimbra M.A., 2012, Coffee melanoidins: structures, mechanisms of formation and potential health impacts, Food Funct., 3, 903–915.

Murthy P.S., Naidu M.M., 2012, Sustainable management of coffee industry by-products and value addition: A review, Resour. Conserv. Recycl., 66, 45–58.

Panusa A., Zuorro A., Lavecchia R., Marrosu G., Petrucci R., 2013, Recovery of natural antioxidants from spent coffee grounds, J. Agric. Food Chem., 61, 4162–4168.

Wu F.C., Tseng R.L., Huang S.C., Juang R.S., 2009, Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: A mini-review, Chem. Eng. J., 151, 1–9.

Zuorro A., Di Battista A., Lavecchia R., 2013, Magnetically modified coffee silverskin for the removal of xenobiotics from wastewater, Chemical Engineering Transactions, 35, 1375–1380.