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Adsorption of anthocyanins using clay–polyethylene nanocomposite particles



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ABSTRACT

Clays are often used in adsorption processes due to their remarkable adsorptive characteristics and high specific surface area. However, a colloidal system is formed when the clay is dispersed in water, leading to difficulties in clay recovery and separation at the end of the process since clay sedimentation is hindered by colloidal forces. The objective of this work was to obtain clay polymer nanocomposites (CPN) comprised of micrometric polyethylene particles presenting clay particles physically adhered to the surface. How the CPN particles interact with the aqueous phase was also investigated, since the adsorption processes are usually carried out in several washing steps.

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1. Introduction

Adsorption is widely used in industrial processes with adsorbent materials generally characterized by their particulate form and high specific surface area (SSA). Clay is a natural, low cost material that plays an important role as an alternative adsorbent medium (Gürses et al., 2004; Kelm et al., 2003; Nayak and Singh, 2007). It has been used to remove contaminants, such as dyes, from industrial effluents (Ghosh and Bhattacharyya, 2002; Harris et al., 2001). When dispersed in water, clays are prone to form a colloidal dispersion mainly due to their small particle sizes (less than 4 μm according to the Atterberg and Wentworth granulometric scales (Carvalho et al., 2000)), ground texture and surface charge (Baik and Lee, 2010; Douch et al., 2009).

The plastic behaviour of clay–water dispersions leads to difficulties in sedimentation and/or separation of the solid adsorbent from the liquid phase in static adsorption systems. On the other hand, continuous processes, such as bed columns, may undergo structural modifications (cracking, preferential ways formation and permeability loss) due to bed swelling, compaction and/or colmatation, resulting in liquid flow instability and incomplete adsorption (Lopes et al., 2005, 2007; Yaneva et al., 1995; Yilmaz and Civelekoglu, 2009).

In order to overcome this difficulty, calcination is generally carried out to form pellets and avoid disruption. However, the high temperatures

result in a remarkable reduction in the clay adsorption capacity (Ghosh and Bhattacharyya, 2002; Lopes et al., 2005, 2007).

In order to find a solution for the above mentioned problems, this work aims to obtain a clay polymer nanocomposite (CPN) composed of clay immobilized on the surface of polymer pellets. The adsorption capacity of the CPN particles in the partial purification of anthocyanins from red cabbage was also tested.

2. Experimental procedure

2.1. Material

The adsorbent media used was Tonsil Terrana 580 FF clay (Süd Chemie). Pellets of high density polyethylene (HDPE, Ipiranga Petroquímica S.A.), HD 7255 LS-L, GE 4960 BR, GD 5150 K, GF 5150 and GM 9450 F were used as support (3 mm average particle diameter, $954 \pm 3 \text{ kg m}^{-3}$ specific mass and softening temperature from 165 to 230 °C). Red cabbage dye was obtained by acidic aqueous extraction from crude red cabbage (Cooper-Driver, 2001; Fan et al., 2008; Jackman and Smith, 1992). Alternatively, an aqueous solution of commercial red cabbage dye (30-WS-P, Christian Hansen Inc.) was prepared.

2.2. Adsorbent characterization

Pastilles of Tonsil Terrana 580 FF clay were analysed by X-ray fluorescence (Philips, model PW). The zeta potential (Zeta Plus) was measured evaluating the electrophoretic mobility of the water dispersed particles by laser diffraction. Clay SSA was measured using liquid nitrogen adsorption (Autosorb-1, Quantachrome) ($T = 77 \text{ K}$) by the Brunauer, Emmett and

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Teller (BET) method. SSA was measured for the crude clay and after thermal treatment (210 °C for 2 h). X-ray diffraction (XRD) (Philips, model Xpert) was carried out to investigate the crystallinity before and after thermal treatment (210 °C for 2 h), as well as to observe possible structural modifications. Co K α radiation ($\lambda = 1.5418 \text{ \AA}$) was used at 40 kV and 30 mA. The scanning conditions were $0.05^\circ \text{ s}^{-1}$ from 10 to 70°.

Changes in the clay morphology during the heating process were observed by thermal gravimetry (TG) and differential thermal analysis (DTA) using a simultaneous thermal analyser model Netzsch STA 409. Samples were heated from about 25 °C up to 320 at a $5^\circ \text{ C min}^{-1}$ heating rate.

2.3. Pellet manufacturing

HDPE pellets were mixed with the clay at a mass ratio of 1:1 (clay/polymer). The system was heated at their nominal softening temperatures for 2 h in an oven. The pellets were then washed and dried to remove the clay that did not stick to the pellets' surface.

2.4. Particle morphology

Scanning electron microscopy (SEM, PHILIPS, model XL-30 at 20 kV) was used to evaluate the surface of the clay polymer pellets before the adsorption step and after the desorption step. Images from both backscattered and secondary electrons were considered. The pellets were immersed in liquid nitrogen and broken in order to show the inner polymeric matrix and the clay layer was evaluated using an appropriate image analyser software.

2.5. Static adsorption experiments

Static experiments were carried out with the clay–polymer particles, mixing 50 mL of a $3 \text{ mg} \cdot \text{mL}^{-1}$ aqueous solution of a commercial red cabbage dye under magnetic stirring for 30 min. The clay mass in each essay was determined. McIlvaine buffer solution (pH 3) was used in the adsorption, ethanol–water mixtures (30% vol/vol) and acetic acid dilutions (5% vol/vol) (Xavier et al., 2008). Desorption was carried out using an ethanol/water/citric acid solution (70:30:5 vol/vol/wt) for 30 min. Dye concentrations in the liquid samples were measured in a spectrophotometer (Spectronic Unicam, USA, model Genesys 10 Vis) at 550 nm. The calibration curve was obtained using the commercial dye.

3. Results and discussions

3.1. Adsorbent characterization

The clay elementary analysis, the dependence of zeta potential on pH at $22 \pm 1^\circ \text{ C}$ and the XRD of the Tonsil Terrana 580 FF clay are shown in Table 1, Figs. 1 and 2, respectively.

Table 1
Average chemical composition of Tonsil Terrana 580 FF clay.

Compounds	Mass (%)
Silicon dioxide (SiO ₂)	53.48 ± 2.86
Aluminium oxide (Al ₂ O ₃)	17.86 ± 2.11
Iron oxide (Fe ₂ O ₃)	8.29 ± 1.07
Calcium oxide (CaO)	2.60 ± 0.21
Sodium oxide (Na ₂ O)	0.12 ± 0.01
Potassium oxide (K ₂ O)	3.25 ± 0.44
Manganese oxide (MnO)	0.18 ± 0.00
Titanium oxide (TiO ₂)	0.90 ± 0.01
Magnesium oxide (MgO)	2.61 ± 0.47
Phosphorus oxide (P ₂ O ₅)	0.34 ± 0.01
Weight loss (T = 950 °C)	10.02 ± 0.88

The high content of iron ($8.29 \pm 1.07\%$) and potassium ($3.25 \pm 0.44\%$) oxides may indicate the presence of illite. Mass losses at 950 °C are mainly due to water, and hydroxyl or hydroxide group decompositions such as Al(OH)₃ and Fe(OH)₃. Volatile compounds, such as organic matter, sulphides, carbonates and sulphates, are also included in that determination (Quantachrome Corporation Catálogo, 2000; Tateo et al., 2006).

The zeta potential shows the superficial charge as a function of the pH of the colloidal systems (Liu et al., 2002). The existence of negative charges on the clay surface in an acid medium is very important when clay is used to adsorb red cabbage anthocyanins from the solution because, in this situation, the dye shows the positively charged flavilium structural form (Brouillard, 1983). The pH of zero potential was 9.56, indicating that the clay is a good material to be used in processes where positively charged adsorbates are used at a pH of less than 9.56. The pH value of clay dispersed in water was 7.8, corresponding to a minimum potential zeta and a maximum adsorption of the flavilium ion.

Seven crystallographic phases were observed in X-ray diffractograms: illite (K(Al Fe)₂AlSi₃O₁₀(OH)₂H₂O – JCPDS 15-603), kaolinite (Al₂Si₂O₅(OH)₄ – JCPDS 06-221), quartz (SiO₂ – JCPDS 05-490), illite–montmorillonite (KAl₄(SiAl)₈O₂₀(OH)₄ xH₂O – JCPDS 07-330), montmorillonite (Na_{0.3}(Al,Mg)₂Si₄O₁₀(OH)₂ xH₂O – JCPDS 13-259), muscovite (KAl₂Si₃AlO₁₀(OH)₂ – JCPDS 7-25), and calcium and iron oxides (CaFe₄O₇ – JCPDS 12-145) (JCPDS, 1981). Similar peak configurations were shown by the XRD of crude and heated clay, indicating the stability of the mineralogical phases. Magnitude alterations of the peak height were observed after heating at 210 °C for 2 h, probably due to the loss of water and organic material from the structure.

The values found for N₂ adsorption at 77 K before and after thermal treatment at 210 °C for 2 h are shown in Table 2. For heating up to 320 °C, the mass variation observed in the thermal gravimetric analyses (TG and DTA) of the sample is shown in Fig. 3.

The water or organic matter losses (about 4%) can be responsible for the changes observed in the physical properties of Tonsil Terrana 580 FF clay. During the heating process, mass loss began at approximately 60 °C and reached around 80% of the total at 160 °C, indicating that it was probably due to evaporation of free water found between the clay layers. The DTA showed endothermic effects related to the observed mass loss, showing a peak at 100 °C that corresponds to the water evaporation temperature. It was observed that the external surface of the clay darkened after heating, probably due to the oxidation reactions of the external organic matter adhering to the clay particles. According to Reed (1998) these reactions are followed by an increase in the active sites available to the adsorption process since an increase in the adsorption capacity is usually observed.

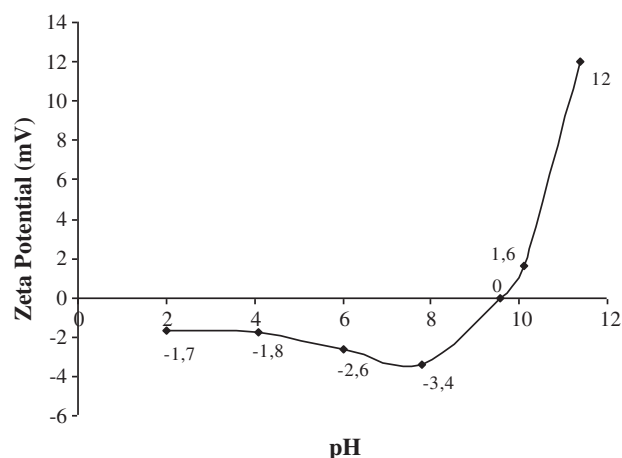


Fig. 1. Zeta potential of Tonsil Terrana 580 FF clay at 22 °C.

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