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A N I N T E R N A T I O N A L J O U R N A L

Adsorption of Natural Dyes on Clay Fixed on Polymers

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ABSTRACT

The main purpose of this work was to produce a pellet to minimize undesirable effects in fixed beds, such as colmatation, through clay fixation on the surface of polymeric particles. Preliminary experiments were carried out by heating the clay, namely Tonsil Terrana 580FF, in order to observe variations on its capacity to adsorb anthocyanins derived from red cabbage. Clays was fixed on five samples of high density polyethylene (HDPE) at 180°C -210°C for two hours. The morphological analyses of the resulting particles were accomplished through Scanning Electron Microscopy (SEM). The experiments demonstrated an increase on clay's adsorptive capacity of 15.65% at 120°C for 30 hours and 16.80% at 170°C for two hours. The SEM analysis showed that the clay particles adhered on the external surface of the pellets .These results show that it is possible to obtain polymeric pellets using HDPE coated with clay.

Key words: Adsorption; clay; polymer; anthocyanin, red cabbage

INTRODUCTION

Food industry has used dyes of synthetic origin, but progressive restrictions given by legislation (FAO/WHO, FDA and of Secretaria Nacional de Vigilância Sanitária do Ministério da Saúde do Brasil) on red amaranto and some blue dyes contributed to stimulate the research natural and non-toxic dyes. This matter has leading to an increasing interest in natural dyes as a substitute of synthetic ones in recent years, due to their properties, especially considering their beneficial effects on biological systems (Aruoma, 2003; Renaud and De Lorgeril, 1992).
Anthocyanins are natural dyes that belong to the flavonoid group (Peterson and Dwyer, 2000). They are water soluble, and are responsible for the blue, red, violet and purple colorations in several plants (Stringheta, 1991). These dyes can be partially or totally purified by adsorption process. Among the adsorbents normally used in this process, clay has been an important material due to its good sorption capacity. Clays are characterized by particles with a fine and very porous structure. Its porosity may reach values as high as 50% of the whole volume of the particle (Geankoplis, 1993). Clay also presents the swelling phenomenon that happens when particles of clay are humidified (Van Olphen and Fripiat, 1979; Neuman et al, 2000). Continuous processes in the fixed bed frequently use adsorbent materials that

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cause some difficulties such as colmatation, head losses and compactation of the bed.
This work aims to accomplish a new technology with the purpose to achieve a new adsorbent material that could minimize these difficulties. Tonsil Terrana 580FF clay was adhered on polymeric beads of high density polyethylene (HDPE), for subsequent use in separation and purification by adsorptive processes of natural dyes.

MATERIAL AND METHODS

Material

Tonsil Terrana 580FF clay was supplied by Süd Chemie do Brasil Ltda. It is smectitic natural clay and its chemical composition and physical properties are presented in Table 1. Commercial dye from red cabbage was supplied by Christian Hansen Comércio e Indústria Ltda. Five samples of high density polyethylene (HDPE) pellets (mean diameter of 3 mm) were supplied by IPIRANGA PETROQUIMICA S.A and Solvay Polietileno Ltda, Brazil.

Thermic treatment of the clay

Tonsil Terrana 580FF clay was thermically treated in an oven with temperatures varying from 60 to 170°C for two hours, and at 120°C at the heating times of 1, 2, 3, 5, 10, 24 and 30 hours. Static experiments using anthocyanin from red cabbage were made to test the variation of the adsorption capacity of the clay

Table 1 - Physical properties and chemical composition of Tonsil Terrana 580FF clay

Properties	Quantification
Apparent specific mass (Kg. m^{-3})	850-950
Free acidity (% H_2SO_4)	--
Humidity (humid basis)	6.0-10.0
Average Chemical Composition	**% in Mass**
Silicium Oxide	42.0 -60.0
Aluminum Oxide	16.0 -20.0
Iron Oxide	6.0 -10.0
Calcium Oxide	1.0 -8.0
Magnesium Oxide	1.0 -8.0
Titan Oxide	0.4 -3.0
Potassium Oxide	0.3 -3.0
Sodium Oxide	0.3 -3.0

Source: Süd Chemie do Brasil Ltda.

Pellets manufacturing

HDPE beads were mixed with clay and heated at the nominal softening temperatures of 180, 190 and 210°C for two hours in an oven. The pellets were washed and dried to get off the excess of clay's particles that did not stick on the polymer. The ratio mass of clay/polymer was 1:1.

Static adsorption experiments

Static experiments were carried out with a known mass of clay, or pellets of clay, mixed with 50 mL of a solution of 3 mg mL^{-1} of the commercial dye from red cabbage on a magnetic stirrer for 30 minutes. Buffer solutions were used to maintain the pH at the desired value (Lopes, 2002). Desorption was done for 30 minutes using ethanol, water and citric acid (70:30:5 V/V/w). The determination of the dye concentration in the liquid samples was made using a spectrophotometer at 550 nm. Concentration was obtained by using a standard curve of the commercial dye.

Particle's morphology

The images used to observe morphology of the particles was obtained through Scanning Electron Microscopy (SEM). Liquid nitrogen was applied to rupt and promoted a good exposure of the polymeric matrix. SizeMeter® Software was used to evaluate the clay's thickness adhered on the external surface of the polymer beads.

RESULTS AND DISCUSSION

Adsorption capacity of Tonsil Terrrana 580 FF clay

Fig. 1 shows the variation of the adsorbed dye on clay as a function of the treatment temperature at an initial concentration of 3.0 mg mL^{-1}. Standard deviations are shown in the figure. There was a clear increase in the mass of dye adsorbed. Between 60-170°C the difference in the adsorbed mass was 16.8%. However a mass loss of clay was observed at different temperatures (Fig 2). This could be due to the humidity loss, and to the degradation of the organic matter. Minimum and maximum values were 95.3±0.1% and 92.4±0.5%, when temperature increased to 110°C, and showed a stabilization around 93%.

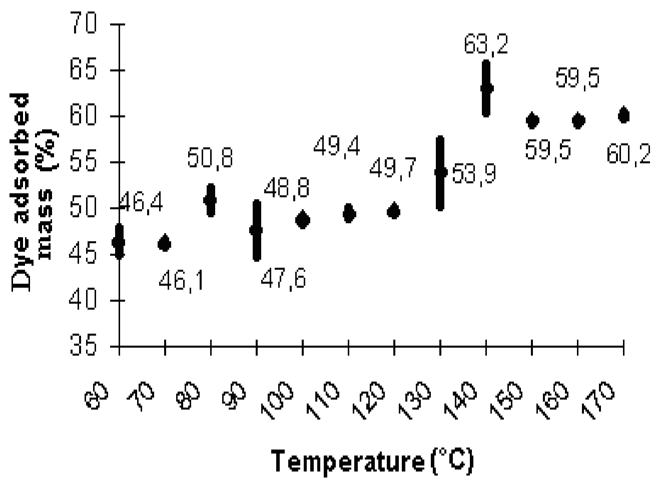

Figure 1 - Clay adsorption capacity after thermic treatment.

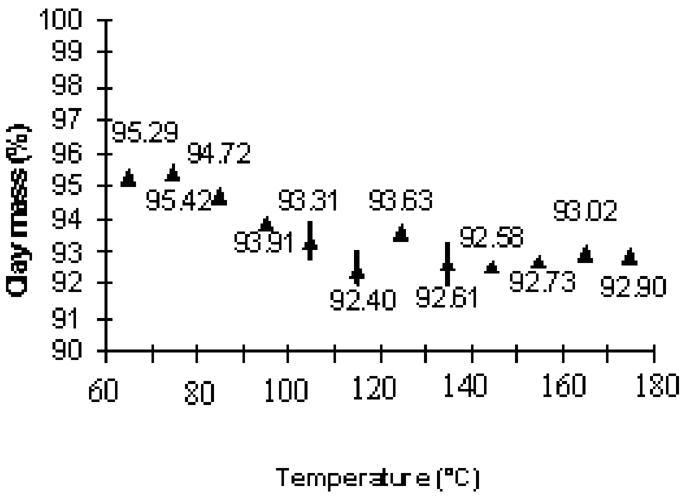

Figure 2 - Mass loss of clay.

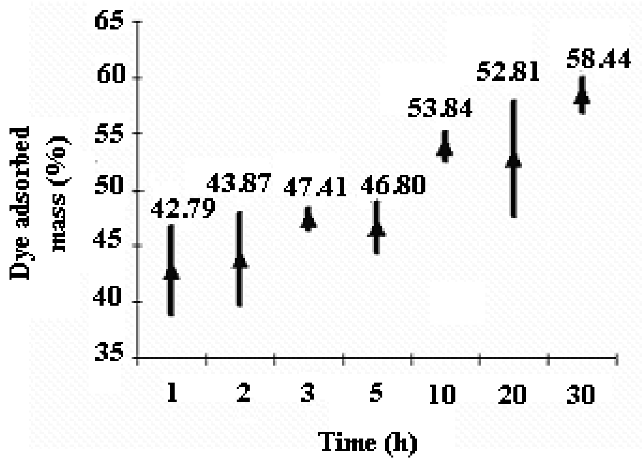

Figure 3 - Dye adsorbed mass at 120°C

Thermic treatment had a beneficial effect on the adsorption capacity of the clay. Fig. 3 shows the kinetics of clay adsorption at 120ºC. An increase of 15.65% in the dye adsorbed mass was observed when the heating time increases from 1 to 30 hours.

It was observed that clay darkened at the particles surface, probably due to oxidation reactions caused by the oxygen and high temperature. This phenomenon was also observed by Reed (1995). Oxidation of the organic matter adhered to the clay particle was probably followed by an increasing in the active sites available for adsorption. This explained the increase of clay adsorptive capacity when it was thermically treated.

Manufacturing the pellets

Tests of fixation of clay on surface of HDPE made in five samples with different specific mass, temperature were chosen considering technical specifications of the supplier (Table 2), which showed that for similar HDPE mass, sample 4 presented the higher adhered mass of clay. However, sample 4 showed also a strong melting, with interparticle adhesion, resulting in a grainy structure. Many individual pellets also deformed into a cap, loosing its spherical form. Results indicated sample 5 as a possible support of adsorbents.

Static adsorption experiments

Adsorption experiments of natural dye were conducted using pellets from sample 5, which presented better performance during fixation process. Table 3 shows the results for an initial concentration of 1 $mg.mL^{-1}$. Apparenth with the increase in the mass of clay adhered on HDPE rises, the dye adsorbed also increases, approximately in a linear way. The best adsorption was found for 20.0 g of pellets of the sample 5. Around 67% of the dye mass initially present in the solution was adsorbed, showing that the pellets had a good performance in absorbing anthocyanins of red cabbage.

Table 2 - Characteristics and results for the samples of obtained *pellets* (clay+ polymer).

Sample	$\rho_{polymer}$ (g/cm^3)	Temperature (°C)	Clay adhered ($g\ g^{-1}$)
1	1.000	180	0.092
2	0.946	190	0.083
3	0.948	190	0.100
4	0.952	210	0.135
5	0.954	210	0.119

Table 3 - Adsorption static experiments on pellets

Pellets (clay+polymer)	*Pellets* mass clay+polymer (g)	Clay mass (g)	Percentile of adsorbed dye mass (%)
	5.00	0.595	14.00
Sample 5	10.00	1.188	35.88
	15.02	1.787	49.01
	20.00	2.380	67.61

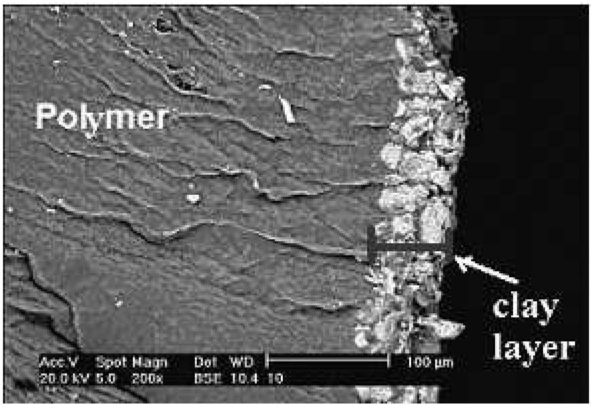

Figure 4 -Polymer's particle with clay adhered on the surface (magnification 200 x).

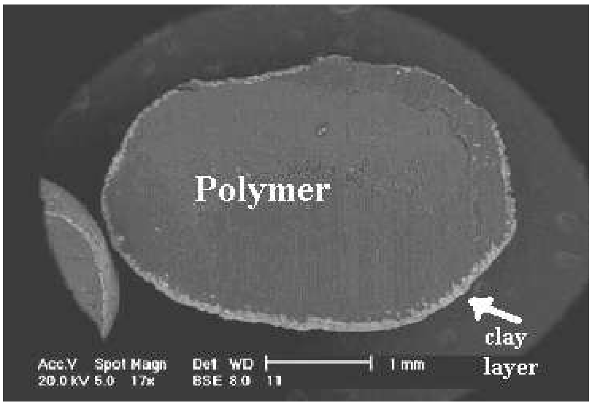

Figure 5 - Polymer's particle with clay after desorption process of natural dye (magnification 20x).

Particle's morphology

Images from Scanning Electronic Microscopy with magnification of 200 and 20 times were taken from the pellets before and after adsorption process. Fig. 4 shows a micrograph of a cut particle with fixed clay on the surface. It was seen that clay inserted on the surface (HDPE permeating the layer of clay particles). This confirmed that fixation occurred because the melting of HDPE allowed clay to mix with the polymer. The control of the time and temperature on a specific polymer determines how much clay can be inserted into beads, and consequently how many sites stay available for adsorption. It is important to consider that heat also increases the

adsorption capacity of the clay, and a possible combined effect occurs when the pellet is formed.
Layer thickness was evaluated using tree particles. Thirty measures were taken from each one. The mean value found was 55.848 ± 6.729 µm.
Fig. 5 shows the micrograph of the pellets after the dessorption process of dye. A diminution of the layer thickness was observed, although a significant part of the particles of Tonsil Terrana 580 FF clay remained on the HDPE beads surface. Thickness layer measured was 28.354 ± 8.226 nm. It was around 50% of the clay layer after the desorption process.

CONCLUSIONS

Thermal treatment increased the adsorption of clay about 15%. Manufactured pellets presented a homogeneous fixation on the clay surface. It was observed that layer thickness was reduced around 50% after the adsorption-dessorption process. Some advantages in using the pellets of HDPE-clay with regard to the original adsorbent were noted, such as sedimentation and separation in static process happened quickly and easily, without need of flocculant addition and/or use of centrifugation.

RESUMO

O objetivo deste trabalho foi estudar formas de minimizar efeitos indesejáveis como a colmatação em leitos constituídos de argila através de sua fixação sobre a superfície de partículas poliméricas. Foram realizados ensaios preliminares aquecendo a argila Tonsil Terrana 580FF em estufas para se observar a variação da sua capacidade de adsorção de antocianinas de repolho roxo. Posteriormente, foram utilizadas 5 amostras de polietileno de alta densidade para a fixação da argila a temperaturas de 180°C-210°C durante 2 horas. As análises morfológicas das partículas obtidas foram realizadas através de microscopia eletrônica de varredura. Os experimentos preliminares demonstraram um incremento máximo de 15,65% na capacidade adsortiva da argila (120°C, 30 horas) e 16,80% (170^{o}C, 2 horas). Estes resultados mostram que é possível obter *pellets* com depósito de adsorventes de fina granulometria fixados superficialmente.

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