CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
 ISBN 978-88-95608-00-6

Modelling The Batch Adsorption Of Red Cabbage Anthocyanins On Clay-Polymer Composites

Lopes, T.J.; Gonçalves, O.H; Quadri, M.G.N.*; Machado, R.A.F.; Quadri, M.B.

Chemical Engineering Department – Federal University of Santa Catarina - University Campus, Trindade, PO box: 476 - CEP: 88040-900 - Florianópolis - SC - Brazil
*E-mail: mara@enq.ufsc.br

Clay particles are frequently used in adsorption processes with aqueous solution, but the formed colloidal dispersion is responsible for several phenomena that hinder the flow. To overcome these problems, this work deals with adsorption experiments carried out using an adsorptive media prepared with clay immobilized on the surface of polymer pellets. Essays were carried to adsorb red cabbage commercial dye, and the composite showed a good performance, added by an easy separation from the liquid phase. A diffusive and convective mass transfer model associated to Langmuir adsorption isotherm described well the experimental data.

1. Introduction

Food industry has used dyes of synthetic origin, but progressive restrictions in legislation (World Health Organization (WHO), Food and Drug Administration (FDA) and State Health Department of Brazil) on red amaranth and some blue dyes contributed to stimulate the processing research of natural and non-toxic dyes. The increasing interest of natural dyes as a substitute of the synthetic ones are also due to their properties, especially considering their beneficial effects on biological systems (Aruoma, 2003; Renaud and De Lorgeril, 1992).
Anthocyanins are natural dyes belonging to the flavonoid group (Peterson and Dwyer, 2000). They are soluble in water, and are responsible for the blue, red, violet and purple colors in several plants. For industrial purposes, they must be extracted and partial or totally purified. Adsorption is a viable process as shown by Coutinho et al. (2004).
Clay is a cheap material with a good sorption capacity that can be used to partially purify red cabbage anthocyanins (Lopes, 2002). It is characterized by particles with fine and porous structure, and swells when their particles are humidified (Van Olphen and Fripiat, 1979; Neuman et al, 2000). Some difficulties occur when colloidal dispersions of clay must sediment in batch systems. In order to overcome these problems, a clay-polymer composite was recently developed (Lopes et al., 2005).
This work aims to apply the clay-polymer composite in the partial purification of red cabbage anthocyanins. For this purpose, static adsorption experiments were developed and modelled.

2. Material and Methods

2.1 Material

Tonsil Terrana 580FF clay (Süd Chemie do Brasil Ltda) is smectitic natural clay with chemical composition and physical properties presented in Table 1. Commercial dye from red cabbage was supplied by Christian Hansen Ltda. Polystyrene beads, 0.71 mm mean diameter, were produced in the laboratory (Control Process Laboratory, Federal University of Santa Catarina, Brazil) using polymerization in styrene suspension. Di-benzoil peroxide (BPO) was used as a chemical initiator, and polivinilpirrolidone (PVP) as stabilizing agent. Expandable polystyrene beads (EPS) were previously dissolved in the monomer phase. The average molecular weight was determined through viscosimetry using toluene as solvent, as described by Bishop (1971).

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

PROPERTIES	QUANTIFICATION
Apparent specific mass (Kg m^{-3})	850-950
Superficial area BET (m^2 g^{-1})	112.3
Humidity (humid basis)	6.0-10.0
Average Chemical Composition (% in Mass)	
Silicium Oxide 42.0 – 60.0	Magnesium Oxide 1.0 – 8.0
Aluminum Oxide 16.0 – 20.0	Titan Oxide 0.4 – 3.0
Iron Oxide 6.0 – 10.0	Potassium Oxide 0.3 – 3.0
Calcium Oxide 1.0 – 8.0	Sodium Oxide 0.3 – 3.0

2.2 Clay-polymer composites manufacturing

Clay mixed to polystyrene (MW 160,000 g $gmol^{-1}$) beads were heated at the nominal softening temperature of 210°C for two hours in an oven. The pellets were washed and dried to get off the excess of Tonsil Terrana 580 FF clay not stacked on the polymer. The ratio mass of clay/polymer used was 1:1.

2.3 Static adsorption experiments

Static experiments were carried out with a known mass of clay-polymer composites, mixed with 50 mL of solution of red cabbage commercial dye, and the pH was adjusted to 3.0 with McIlvaine buffer solution. Dye concentration was measured in a spectrophotometer at 550 nm (Lopes, 2002).

2.4 Scanning electron microscopy – SEM

Scanning electron microscopy was used to evaluate the quality of the composite pellets surface before and after adsorption, and after the desorption step. The microscope (PHILIPS, model XL-30) operates at 20 kV with a tungsten source. Images from both back scattered and secondary electrons were considered; the pellets were broken using liquid nitrogen to show the inner polymeric matrix. Image analysis to evaluate and quantify the clay layer was accomplished using the software SizeMeter® (Control Process Laboratory in Federal University of Santa Catarina, Brazil).

2.5 Modeling the batch adsorption of red cabbage anthocyanins

A model considering simultaneous internal diffusion and convection at the particle surface was used to describe the experimental data. Equation 1 is the differencial mass balance at the spherical particle.

$$\varepsilon_p \frac{\partial C_i}{\partial t} + \rho_d \frac{\partial q_i}{\partial t} = D_{ef}\varepsilon_p \left(\frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r}\frac{\partial C_i}{\partial r} \right) \quad (1)$$

Initial condition: $t=0\ ;\ C_i = 0,\quad q_i = 0$ (1.a)

Boundary conditions: at the center of the particle: $r=0; \frac{\partial C_i}{\partial r} = 0$ (1.b)

at the surface: $r=R\ ;\ \frac{\partial C_i}{\partial r} = \frac{k_{conv}}{D_{ef}}\left(C^{\infty}(t) - C_i\right)$ (1.c)

where ε_p is the particle porosity; C_i is the dye concentration at the liquid phase in the internal particle pores; ρ_d is the particle specific mass; q_i is the dye concentration in the solid phase; D_{ef} is the effective diffusion coefficient; t is the time; r is the radial coordinate; C^* is the dye concentration in the liquid phase at the inner of the pores particles at the equilibrium; R is the particle radius; k_{conv} is the convective coefficient of mass transfer; $C^{\infty}(t)$ is the bulk concentration.
The Freundlich and Langmuir models were tested to represent the adsorption isotherm. The mean concentration history (Equations 2 and 3) given by the model is obtained by integration of the concentration profile in the particle (Equation 1). The models of Freundlich and Langmuir were tested to describe the adsorption isotherm.

Applying the Freundlich model:

$$\overline{C}(t) = C_0^{\infty} - \frac{3}{R^3}\int_0^R \left(\varepsilon_p + \rho_d k n C_i^{n-1}(t)\right) C_i(t) r^2 dr \quad (2)$$

Applying the Langmuir model:

$$\overline{C}(t) = C_0^{\infty} - \frac{3}{R^3}\int_0^R \left(\varepsilon_p + \frac{q_0 b}{(1+bC_i(t))^2}\right) C_i(t) r^2 dr \quad (3)$$

where C_0^{∞} is the bulk concentration at the time t=0.

The above equation system was solved by the finite difference method, observing the unicity solution criterion, numerical convergency and satisfied mass balance. The computational implementation was made by Quadri (2001).
It was supposed that:

- the particles are rigid, homogenous, uniform and spherical;
- the dye-solvent mixture is an ideal solution external to the particle, and is represented by the bulk concentration;
- a correction factor considering the mass clay layer proportion in contact with the fluid medium. This parameter was estimated by fitting the model to the experimental data.

3. Results and Discussion

3.1 Particle's morphology

Images from Scanning Electronic Microscopy with magnification of 200 times were taken from the pellets before and after adsorption process. Figure 1 shows a micrograph of a cut particle with fixed clay on the surface. It was seen that clay inserted on the

surface (PS permeating the layer of clay particles). This confirmed that fixation occurred because the melting of PS 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 146.5 ± 7.4 μm.

Figure 2 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 PS beads surface. Thickness layer measured was 123.8 ± 7.1 μm.

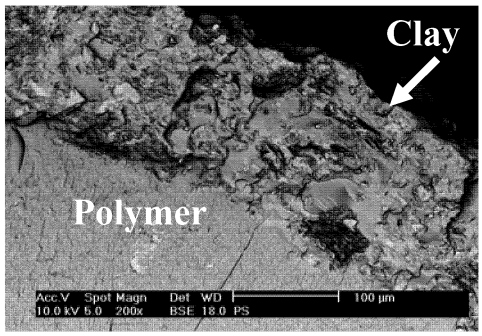

Figure 1: Polymer's particle with clay adhered on the surface (magnification 200x).

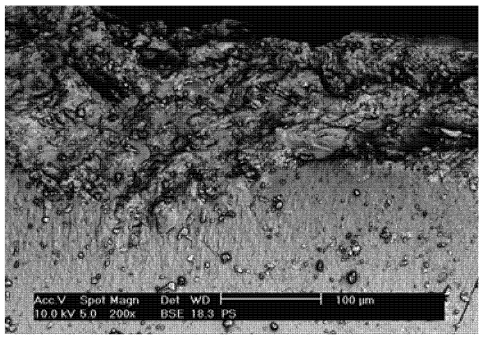

Figure 2: Polymer's particle with clay after desorption process of natural dye (magnification 200x).

3.2 Modelling batch essays

Table 2 shows the experimental imposed parameters to the model used to simulate the red cabbage comercial dye adsorption in the batch experimental data with the clay-polystyrene composite. Isotherms were obtained at about 25ºC. Table 3 shows the fitted parameters in the adsorption process: kinetics and isotherms.

Table 2: Experimental conditions and model parameters used in the batch adsorption process.

Inlet values	**1**	**2**	**3**	**4**	**5**	**6**
C_0 (mg mL^{-1})	1	1	1	5	5	5
Particle mean radius (cm)	0.011	0.011	0.011	0.011	0.011	0.011
ε_p	0.5	0.5	0.5	0.5	0.5	0.5
Composite mass (g)	1	5	10	1	5	10
Estimated clay mass (g)	0.304	2.128	3.04	0.304	2.128	3.04
Correction factor	0.69	0.69	0.69	0.69	0.69	0.69
Corrected clay mass (g)	0.2097	1.468	2.097	0.2097	1.468	2.097
Composite mean radius (cm)	0.0152	0.0152	0.0152	0.0152	0.0152	0.0152
ρ_d (g cm^{-3})	1.18	1.18	1.18	1.18	1.18	1.18

Table 3: Fitted parameters to experimental kinetics and isotherms.

Freundlich isotherm – fitted parameters						
k	401.31	141.43	92.978	401.31	141.43	92.98
n	0.4038	0.5089	0.4404	0.4038	0.5089	0.44
R^1	0.9171	0.9914	0.9899	0.9171	0.9914	0.99
Langmuir isotherm – fitted parameters						
q_0	1038.2	348.54	158.86	1038.2	348.54	158.86
b	0.6373	0.7581	1.8371	0.6373	0.7581	1.84
R^1	0.9668	0.9930	0.9882	0.9668	0.9930	0.99
Kinetics – fitted parameters						
K_{conv} ($x10^{-4}$) (cm s^{-1})	80.8	4.32	3.68	80.8	4.32	3.68
D_{ef} ($x10^{-5}$) (cm^2 s^{-1})	1.025	1.45	2.11	0.102	0.05	0.06
Biot	11.982	0.453	0.264	120.40	12.16	9.32
*Error (%)	0.913	0.342	0.208	0.913	0.316	0.42

*Mass balance accumulated percentual error. [1]R in this table is the determination coefficient.

Table 3 shows that the best fit was obtained using the Langmuir model. The sensibility analysis of the K_{conv} and D_{ef} parameters shows that the K_{conv} variation has a significant influence on the model fitting.

Literature reports values of 0.26 to the Biot number for this system (Lopes, 2002). Such value is characteristic of a dye transport phenomenon controled by the resistence external to the particle. The most part of the process was an instantaneous adsorption, what can be explained by a very small internal resistence to the diffusion due to the small diameter, around 7 micra, and a high porosity, of about 53%, of the particle.

Table 2 shows that the Biot number decreases as the solid mass increases, probably due to the difficulty to shake the system, since the dye volume solution is the same for all cases. For that reason, the convective coefficient of mass transfer, Kconv, tends to decrease.

Figures 3 to 5 show the experimental adsorption kinetics and isotherms of the red cabbage commercial dye in a pH 3.0 McIlvaine buffer solution. The model fitted curves are also showed. The obtained adsorption curves in Figure 3 indicates a reversible process.

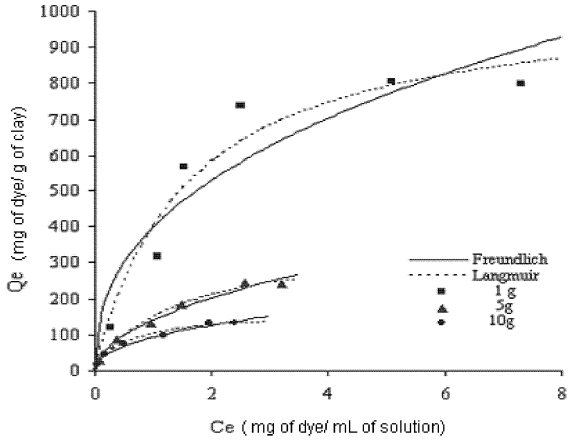

Figure 3: Equilibrium isotherms of red cabbage comercial dye on clay-polystyrene composite.

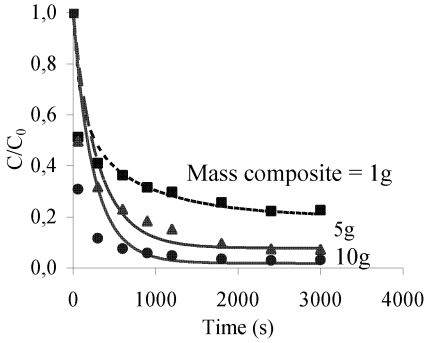

Figure 4: Modelling and experimental adsorption kinetics of red cabbage comercial dye on clay-polystyrene composite (C_0= 1 mg mL^{-1}).

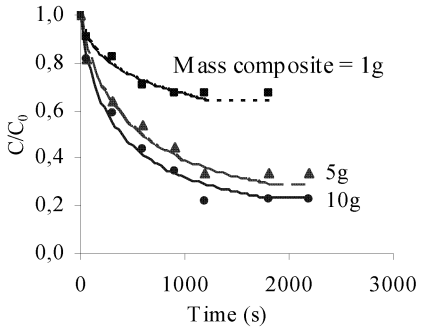

Figure 5: Modelling and experimental adsorption kinetics of red cabbage comercial dye on clay-polystyrene composite (C_0= 5 mg mL^{-1}).

The kinetic step of the anthocyanin adsorption on clay was relatively quick for the three cases presented for initial dye concentration of C_0= 1 mg mL^{-1} (Figure 4). The model can not describe the concentration decrease in the first 600 s. This is probably due to the great number of active adsorption sites and small resistence to the dye transport.

4. Conclusions

Manufactured pellets presented a homogeneous fixation on the clay surface. Some advantages in using the pellets of PS-clay with regard to the original adsorbent were noted, such as quick and easy sedimentation and separation in static process without need of flocculant addition and/or use of centrifugation.
The mass transfer model considering adsorption can, with little limitation, describe well the adsorption of the red cabbage commercial dye on the clay-polystyrene composite.

5. References

Aruona, O. I., 2003, Mutation Research, 523-524, 9-20.
Bishop, R. B., 1971, Practical polymerization for polystyrene. Cahners Publishing Inc.
Coutinho, M.R., Quadri, M.B., Moreira, R.F.P.M., Quadri, M.G.N., 2004, Separation Science and Technology 39 (16), 3769–3782.
Lopes, T.J., 2002, Adsorção de Antocianinas do repolho roxo em argilas. Universidade Federal de Santa Catarina, Florianópolis, Brazil; Masters Thesis. (in Portuguese)
Lopes, T.J., Gonçalves, OH, Barros, R.B., Capelli, F.C.R., Machado, R.A.F., Quadri, M.G.N., Quadri and M.B., 2005, Braz. Arch. Bio. Tech., 48, 275-280.
Neumann, M. G.; Gessner, F.; Cione, A. P. P.; Sartori, R. A. and Cavalheiro, C. C. S., 2000, Química Nova, 23(6), 818-824 (in Portuguese).
Peterson, J.and Dwyer, J., 2000, J. Food Composition and Analysis, 13, 441-454.
Quadri, M.B., 2001, Contribution of irreversible fixation to the stagnant volumes model. Non published, E-mail: m-quadri@enq.ufsc.br
Renaud, S. and De Lorgeril, M., 1992, The Lancet, 339(8808), 1523-1526.
Van Olphen, M. and Fripiat, J. J., 1979, Data handbook for clay materials and other non-metallic minerals. Oxford : Pergamon Press. 346 pp.