Thesis Title	Preparation of Activated Kaolin for Bleaching Rice Bran Oil and Synthetic Kaolinites to Assess Sorption Properties of these Particles in Relation to their Morphology
Thesis Credits	36
Candidate	Miss Lei Lei Aung
Thesis Advisors	Assoc. Prof. Dr. Paitip Thiravetyan Dr. Sabine Petit
Thesis Co-advisors	Dr. Emmanuel Tertre Asst. Prof. Dr. Niramon Worasith Lect. Dr. Parinda Suksabye
Program	Doctor of Philosophy (double badged degree)
Field of Study	Biotechnology/ Terre solide et enveloppes superficielles
Division	Biotechnology/ Gay-Lussac
Faculty	School of Bioresources and Technology (KMUTT)/ Sciences Fondamentales et Appliquées, Institut de Chimie des Milieux et Matériaux de Poitiers (Université de Poitiers)
Academic Year	2014

Abstract

The dissertation consists of two main parts; the first part is devoted to the effect of physical/thermal and chemical activation of kaolin on bleaching of rice bran oil. In this study, samples were prepared from natural Ranong kaolin. This study focused on the effects of both thermal treatment (from 100 to 900°C) and chemical activation (sulfuric acid, hydrochloric acid, citric acid and oxalic acid using different acid concentrations or different clay/acid ratio) on the capacity of kaolins to bleach rice bran oil. When kaolin was treated with high temperature (>100°C) prior to reflux and with a high acid concentration during reflux, the kaolinite structure was partially or completely destroyed associated to a dramatic leaching of alumina, and amorphous silica dominated the samples. The measured maximum bleaching capacity obtained was not consistent with the highest specific surface area and pore volume; rather, it depended on the alumina contents in the samples. Thus, the partial preservation of the kaolinite structure is crucial to obtain an appropriate bleaching capacity of kaolin. This is directly related to the preservation of the aluminol sites present at the kaolinite surface. XRF analysis showed that the alumina contents of 28-34% were values to reach in order to obtain optimum bleaching capacities of kaolin, independently of the different acid used. Finally, optimum bleaching of ~83%, ~82% and ~81% were achieved by grinding the kaolin prior to reflux with low acid concentration of hydrochloric acid (0.5 M), sulfuric acid (0.3 M) and citric acid (0.5 M), respectively with clay/acid ratio of 1:50.

The second part of the thesis aims to elucidate the influence of morphology of kaolinites on their sorption properties. For that, Na^+/H^+ sorption isotherms in water saturated conditions of synthetic kaolinites and natural well crystallized kaolinite, called KGa--1b commercialized by the Clay Mineral Society, were performed and interpreted. Kaolinites used in this study were hydrothermally synthesized from partially crystallized kaolinite as a function of different final pH (pH_F) ranging from 0.8 to 8.3. Results obtained for KGa--1b were compared with data obtained in literature for this mineral, in order to fully validate this approach. This study found that cation exchange capacity, due to both isomorphic substitutions in the crystals (permanent charge), and silanol and aluminol edge sites were highly variable. Typically, CEC at pH=9 varied from ~0.8 cmol$_c$/kg for well crystallized kaolinite (pH$_F$ 0.8) to ~33 cmol$_c$/kg for disordered lath-shaped kaolinite (pH$_F$ 8.3). Na$^+$/H$^+$ sorption isotherms were obtained for all synthetic kaolinites as a function of pH ranging from pH 3 to 11. Results showed that sorption of Na$^+$ increases dramatically with pH. Typically for all kaolinite samples except for the one synthesized at pH$_F$=8.3, Na$^+$ sorption is rigorously equal to zero when pH<7, indicating no permanent charge in the samples (in contrast to natural KGa--1b kaolinite), and increases when pH>7 due to sorption on edge sites. The amount of dissolved silica measured during Na$^+$/H$^+$ isotherm is higher for experiments performed with kaolinites synthesized in basic conditions (for pH$_F$ 7.4 and pH$_F$ 8.3) than for kaolinites synthesized in acid conditions (for pH$_F$ 0.8 and pH$_F$ 3.3). These latter results lead to conclude that sorption site density can be considered constant when pH is between 4 and 10, independently of the morphologies of particles. In this context, a thermodynamic modeling procedure using a complexation model was applied to interpret the data obtained with hexagonal- and lath-shaped particles. During this procedure, selectivity coefficient between Na$^+$ and H$^+$ cations were obtained considering the total edge site densities calculated from lateral specific surfaces estimated for synthetic kaolinites and crystallography data. Results showed that the Na$^+$/H$^+$ selectivity coefficient depends on the kaolinite's size/morphology since for hexagonal-shaped particles a log Kc(Na$^+$/H$^+$) equal to -5.5 was required to interpret experimental data, *versus* log Kc(Na$^+$/H$^+$) of -4.7 for lath-shaped particles.

Keywords: Alumina/ Bleaching/ Kaolin/ Kaolinite/ Morphology/ pH/ Rice Bran Oil/ Selectivity Coefficient/ Sorption Isotherm