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ACTIVATED BLEACHING CLAY FOR THE FUTURE

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ACTIVATED BLEACHING CLAY FOR THE FUTURE

Activated bleaching clays, so called because of their ability to remove color bodies from bleach fats and oils, are produced from clays of bentonitic origin. Activation is achieved by subjecting these clays to physical or chemical alteration to increase selective sorption capacities⁽¹⁾.

The future of activated bleaching clays depends upon the ability of producers to recognize the new areas of applications which are arising, and their skill in developing sophisticated active clays to meet new and stringent requirements.

The major portion of activated bentonites are produced for decolorization of oils. New techniques of activation will improve these clays for broader spectrum use.

General properties expected to result from present activation methods are:

1. Modification of hydrophobic-hydrophilic properties and increased available surface area in non-aqueous systems, thereby improving sorption capacity and ability to remove color bodies from oils.

The following additional properties will be expected from future activated clays:

2. High purity of the active clay with interfering impurities totally removed.
3. Increased selective sorption capacity in aqueous systems.
4. Selective chemical reactivity, such as oxidation or hydrolysis. This property is required for removing

or modification of some organic substances in waste water.

Future Methods for Activating Bleaching Clays

Bentonitic clays which are suitable for production of activated bleaching clays contain the essential montmorillonite clay mineral as well as substantial inert impurities. Activation of montmorillonite by acid leaching involves partial dissolution of the octahedral layer. The activity level attainable depends upon the concentration of the montmorillonite. A high activity clay cannot be obtained by acid activation of bentonite containing a low percentage of montmorillonite.

Removal of inert impurities from bentonite to effect concentration of montmorillonite is a method for improving the activity of bleaching clays. A simple technique which can be employed to concentrate certain montmorillonites is dispersion and centrifugation. This process is schematically presented in Figure 1. Sodium bentonites are readily dispersed and respond well to centrifugal separation. This process is inadequate for the more important calcium-magnesium bentonites from which the majority of activated bleaching clays are prepared. These bentonites require special chemical treatments to render them satisfactory for centrifugal concentration. One commercial process employs the addition of ammonium carbonate to the aqueous slurry of bentonite prior to centrifugation⁽²⁾. Figure 2 illustrates this process for obtaining concentrated calcium-magnesium montmorillonite prior to acid activation.

Further purification techniques may be applied to the acid activated montmorillonite. For Example, ion exchange resins may

be used to remove interfering impurities remaining after the acid dissolution and rinsing procedure. The refined activated montmorillonite may be treated additionally by ion exchange to add important reaction promoting cations, for example, the Fe^{+++} ion as an oxidation accelerator. Figure 3 illustrates a typical ion exchange procedure.

A very interesting activation technique involves the replacement of the inorganic cations by tetra-methyl ammonium or tetra-ethyl ammonium cations⁽³⁾. These cations open up the lamellae of the montmorillonite and cause important changes in the ability of the clay to sorb and intercalate organic molecules. These modified clays readily sorb aliphatic and aromatic hydrocarbons. The sorptive capacity is greatly increased by virtue of the increased available surface area resulting from opening of the lamellae. This type of activation renders the bentonite particularly suited for sorption of organic vapors.

Future Applications for Activated Bleaching Clays

1. Decolorization of Fats and Oils:

Decolorization of fats and oils by activated bleaching clays will continue to be important. The more concentrated forms of activated clays should gain greater acceptance. These types of clays, although costlier to produce, have the advantage of greater decolorizing capacity, therefore requiring lower dosages. By virtue of using less clay, less oil is retained, which improves the yield of finished oil and requires less filter capacity.

Improvements of activated bleaching clays are still

necessary for more successful clean-up of dry-cleaning fluids in continuous circuit. This process requires a granular sorbent to allow flow of fluid without excessive back pressure. Generally, activated bleaching clays in granular form have low porosity and do not exhibit their full sorption capacity.

2. Waste Water Renovation:

A. Primary Industrial Effluents

Waste water renovation is the most promising future application of activated clays. Pollution control will require efficient and economical methods for removal of contaminants in industrial waste water. Dissolved or colloidal contaminants present in low concentrations are especially difficult and expensive to remove. Many of these contaminants could be removed economically by activated bleaching clays.

Bentonites sorb or react with certain organic molecules to form organo-montmorillonite complexes (4, 5,6,7,8). Primary, secondary, and tertiary amine salts, as well as quaternary ammonium salts form organo-montmorillonite complexes through cation exchange. Proteins, at or below the isoelectric pH, are rapidly complexed by montmorillonite through cation exchange involving the ionized amino group (9,10,11). These organo-montmorillonite complexes generally form flocced precipitates in water and are easily removed from suspension by filtration, centrifugation, or settling.

Montmorillonite or activated bentonites are able to react with very dilute solutions of these organic substances. Thus, the clay acts as an economical scavenger and offers a technique for renovation of large volumes of contaminated water.

Activated clays are also capable of removing colloidal contaminants from suspension. This is important as many industrial effluents contain colloidal particles.

Bentonite or activated bentonites are anionic and react readily with positively charged colloids. More important, they are also capable of floccing negatively charged colloids. It is not immediately apparent why this should occur. However, it has been shown that this type of flocculation does not occur in the absence of appropriate cations⁽¹²⁾. One explanation is that complex formation occurs in the electrical double layer adjacent to the particles of bentonite in suspension where the counter ion concentration is greater than in the bulk. Complex formation is then followed by attachment of the bentonite to the colloid surface and bridging to cause flocculation⁽¹³⁾.

X-ray diffraction analyses have shown that organic anions do not enter between montmorillonite platelets, but are sorbed on the edges of the clay particles⁽¹⁴⁾. The mechanism of organic anions bonding to the edges of montmorillonite has been considered as an electrostatic bonding of the anion to positively

charged sites on the clay edges⁽¹⁵⁾.

This reaction can be illustrated by the flocculation of negatively charged colloidal polystyrene with a calcium cation activated bentonite. Waste water containing 0.2 to 1% colloidal polystyrene is a typical industrial effluent which can be successfully treated with properly activated clays. Generally, 100,000 to 500,000 gallons of waste water must be treated daily in this type of operation. The waste water stream can be dosed with a 5% suspension of the calcium ion activated bentonite in a continuous metered operation. The resulting flocced polystyrene can then be removed from the waste water stream by continuous screening, filtration, or centrifuging. The renovated water can be dumped or recycled to the plant. Properly controlled, this treatment results in water with near zero turbidity. Also, the treatment does not introduce any harmful residue.

It is interesting to note that sewage colloids have negative charges and the treatment which functions so well in removing colloidal polystyrene from waste water will remove many sewage colloids.

B. Secondary Sewage Disposal Plant Effluent

The occurrence in municipal waste water of organic contaminants resistant to biological degradation offers a major technical challenge for activated bleaching clays. These organic contaminants must be removed to sufficiently purify the water for re-use or to prevent

interference with other stages of treatment.

Separation techniques suitable for removing the refractory organic compounds, occurring in secondary effluents in concentrations of 50 to 100 ppm chemical oxygen demand (COD), will be required. The successful technique must be able to scavenge organics at 3 to 5 ppm concentrations from large volumes of waste water. Sorption is a very effective method of achieving removal of organic substances from aqueous solutions. The challenge to producers of activated clays will be to develop clays which can economically and efficiently accomplish this sorption.

Past tests have indicated that bentonites and certain activated clays were ineffective in sufficiently reducing COD. This was the result of using clays not specifically designed for sorption and reaction in water systems containing organic contaminants. Both the type of bentonite and the method of activation are important in determining the amount of COD reduction.

Data have been obtained demonstrating the effect of bentonite upon the oxidation of hydroquinone in water. Inasmuch as derivatives of polyhydric phenols, such as hydroquinone, are frequently found in waste waters, these data are of particular interest.

Oxidation of hydroquinone, $\text{HO} - \text{C}_6\text{H}_4 - \text{OH}$, results in the formation of a well-defined monomeric product, p-benzoquinone $\text{O} = \text{C}_6\text{H}_4 = \text{O}$, allowing accurate measure of the oxidation reaction.

In this experiment, the montmorillonite fraction of two Wyoming sodium bentonites, designated Type 1 and Type 2, was converted to various homoionic forms by ion exchange. These montmorillonite forms were then added to a 0.5 millimole solution of hydroquinone and air was bubbled through the mixture for 4 hours, 18 hours, and 4 days. The amount of p-benzoquinone formed did not vary with the time periods chosen. Results of this experiment are listed in Table I.

The data obtained indicate a great difference in oxidizing capacity of the two types of montmorillonites. Also, the importance of the exchange ion is demonstrated. The Fe^{+++} ion in exchange positions has a strong influence and tends to equalize the two types of montmorillonites. Also demonstrated is the role of montmorillonite as an active catalyst promoting a chemical reaction which does not proceed appreciably in its absence. The by-products produced from an oxidation reaction promoted through montmorillonite can be sorbed on the montmorillonite, thus further reducing organic contaminants which consume oxygen.

A montmorillonite treated to improve its oxidizing capacity, coupled with its sorption capacity, should be an excellent activated clay for lowering COD of secondary sewage disposal plant effluent.

Summary

Although there will be continued demand for improved activated bleaching clays for decolorizing fats and oils, one future challenge for these activated clays is in the treatment of waste water. The need to specifically design an activated clay for a given application is of paramount importance. Continued cooperation with various industries involving selective sorption problems will be necessary to assist in the design of new activated clays for the future.

TABLE I

Milliequivalents of p-benzoquinone
per 100 grams Montmorillonite

Exchange Ion	Type 1 Montmorillonite	Type 2 Montmorillonite
Fe ⁺⁺⁺	24.40	21.00
Li ⁺	15.30	5.48
Na ⁺	15.30	4.79
K ⁺	12.80	2.03
Ca ⁺⁺	8.94	1.53
Ba ⁺⁺	7.05	1.32
Mg ⁺⁺	5.86	0.92

CONTROL: Air bubbled through solution of hydroquinone without presence of montmorillonite produced no measureable p-benzoquinone.

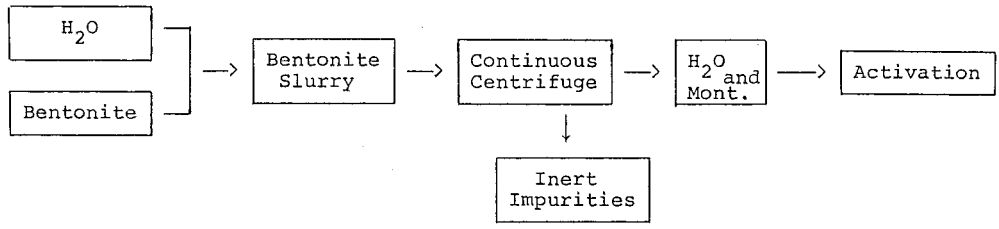


Figure 1

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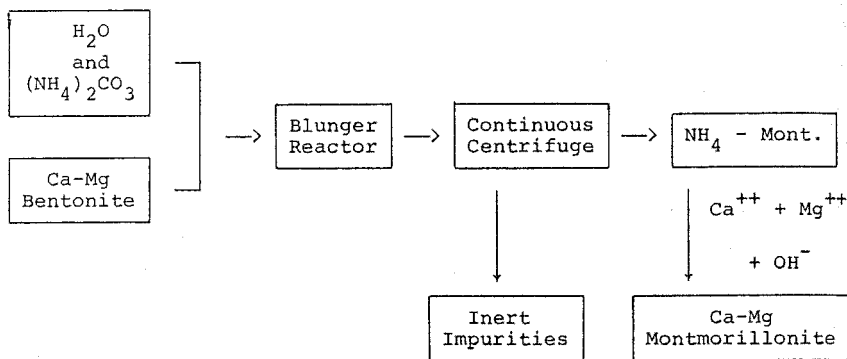


Figure 2

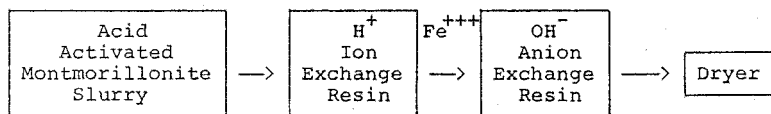


Figure 3