

USE OF INORGANO-ORGANO-CLAYS IN INDUSTRIAL WASTEWATER TREATMENT:

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ABSTRACT:

Inorgano-Organoclays (IOCs), prepared by simultaneous adsorption of a cationic, inorganic polymer and a cationic surfactant on the surface of montmorillonites, have been found to be comparable to activated carbons in their sorption potentials for toxic organics in aqueous streams. The surfactant content of IOCs has been modified to promote differential adsorption of priority pollutants. Experiments with surfactant-modified kaolinites have revealed the importance of the surface orientation of the adsorbed organic carbon. Sorption experiments in actual coal conversion wastewaters have demonstrated that the sorption behavior of IOCs is equal to or better than that of activated carbons.

INTRODUCTION:

Adsorption of trace levels of nonionic, toxic organic molecules from wastewaters is a microseparation process requiring cost-effective and efficient adsorbents. Adsorption as a pre-concentration step in a cascade of unit operations leading to the ultimate destruction of toxic organics is an important component of any wastewater treatment scheme (1). Secondly, discharge streams containing exceedingly low levels of pollutants may require a final polishing step, and adsorption is used under these conditions as well (2). On a much larger scale, physical adsorption in combination with biodegradation (as exemplified by the well known PACT wastewater treatment system) has been shown to be particularly effective in treating wastewaters which are variable in concentration and composition. Thus, a fully developed, modified-clay sorption technology offers the prospects of an inexpensive alternative to activated carbon, which is the current industry standard for above-mentioned uses.

During the past several years, the authors have developed a number of modified montmorillonites, the most prominent of which were cetyl pyridinium montmorillonite (CPC-MONT) and cetyl pyridinium hydroxy aluminum montmorillonite (CPC-HYDAL-MONT) (3- 6). CPC-MONT was a prime example of an organo-clay in which the bulk of the adsorbed organic carbon was localized in the interlayer space between clay lamellae. CPC-HYDAL-MONT, in which both a polycationic hydroxy aluminum moiety (HYDAL) and a cationic surfactant (CPC) were found to bind simultaneously to the modified clay surface, was designated by us as an inorgano-organoclays (IOC). Two major differences between these two modified smectites were the amounts and the orientations of the adsorbed surfactant; mainly in the interlayer space and on the external surface in the cases of CPC-MONT and CPC-HYDAL-MONT respectively. An idealized representation of the structures of these two modified clays is shown in Fig. 1. Previously, we had prepared CPC-MONT and CPC-HYDAL-MONT containing respectively 23 and 17% by weight adsorbed CPC. CPC-HYDAL-MONT was found to be a better adsorbent than CPC-MONT and the greater effectiveness of CPC-HYDAL-MONT was shown to arise from the differences in the surface orientation of the adsorbed surfactant. (6). One of the

objectives of the present study was to optimize the surface concentration of the adsorbed surfactant on CPC-HYDAL-MONT in order to improve its cost-effectiveness. Since kaolinites are known to be non-expanding clays of low CEC, and do not intercalate molecules other than neutral polar ones capable of hydrogen bond formation (7), the adsorbed surfactant would be mainly located on the external surface of the clay. Experiments with two types of CPC-kaolinites were carried out to delineate the effects of such a surface orientation. A comparison between CPC-HYDAL-MONT and powdered activated carbon (PAC) and granulated activated carbon (GAC) was undertaken. Finally, the effectiveness of using CPC-HYDAL-MONT in an actual coal conversion wastewater was examined. In this study, pentachlorophenol (PCP) and benzo(a)pyrene (B(a)P) were used as the target toxic organics.

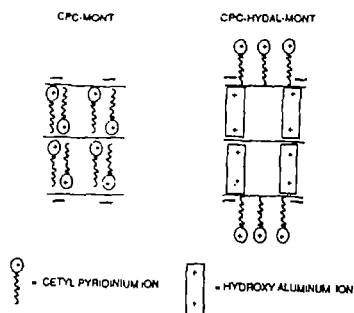


FIG. 1 IDEALIZED STRUCTURAL MODELS OF CPC-MONT AND CPC-HYDAL-MONT.

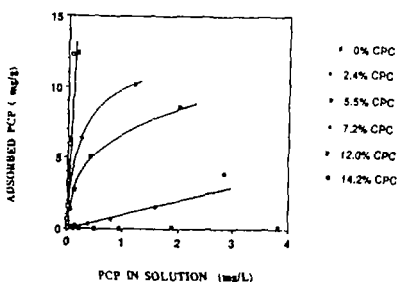
NOTE: In CPC-MONT, CPC is in interlayer space.
In CPC-HYDAL-MONT, CPC ion is mainly on the external surface with the orientation as shown above.

MATERIALS AND METHODS:

Na-montmorillonite and two types of kaolinites, KGA-1 and KGA-2, were obtained from Source Clay Minerals Repository, University of Missouri, Columbia, MO. KGA-1 is a crystalline form of kaolinite with a lower surface area and CEC, while KGA-2 is a more amorphous form having slightly higher values for both these properties. Granulated activated carbon (GAC; Filtrasorb-400) and powdered activated carbon (PAC) were gifts respectively from Calgon Corporation and the Anderson Development Company, Adrian, MI. All other chemicals and reagents were of the analytical grade. Conductivity-grade water available from a Milli-Q water system (Millipore Corporation) was filtered through a Nalgene 0.22 μ m filtration unit prior to use. Coal conversion wastewater was supplied by the Coal Liquefaction facility in Wilsonville, Alabama. 14 C labeled PCP (87000 dpm/ μ g) and 3 H labeled B(a)P (96 dpm/pico gram) were obtained respectively from The Sigma Chemical Co. and The Chemsyn Science Labs.

CPC-HYDAL-MONT containing different amounts of adsorbed CPC and CPC-MONT with 23% adsorbed surfactant were prepared using procedures described elsewhere (6). CPC concentration was assayed spectrophotometrically at 259 nm using a calibration curve obtained by liquid phase organic carbon analysis. The amount of adsorbed surfactant was determined by the difference, which, in many cases was verified by separate solid phase organic carbon assays. With CPC-

FIG. 2 SORPTION OF PCP ON CPC-HYDAL-MONT EFFECT OF ADSORBED SURFACTANT



kaolinites, the highest surface concentration of CPC was found to be 1.8 and 2.7% by weight respectively in the case of CPC-KGA1 and CPC-KGA2. Aqueous solutions of PCP and B(a)P were prepared by blending the respective labeled and unlabeled compounds. An identical procedure was adopted with coal conversion wastewater, which was filtered through 0.22 μm filter prior to use. The initial concentrations of PCP ranged from 0.1 to 5.5 ppm. The corresponding values for B(a)P were 0.1 to 1.2 ppb. All adsorption measurements were carried out in a batch mode in glass vials at 298 K. Details are given elsewhere (6). The average mass balance was around 93%. Experiments with less than 90% mass balance were repeated. Each data point is the mean of a set of four measurements, with a relative error of 10% or less. Sorbent concentrations of 250 ppm were consistently used in this study. Finally, special precautions were taken to minimize the exposure of B(a)P solutions to room light in order to prevent photo decomposition of the solute.

RESULTS AND DISCUSSION:

PCP ADSORPTION: OPTIMIZATION OF ADSORBED SURFACTANT:

The adsorption of pentachlorophenol (PCP) as a function of the surfactant (CPC) concentration on the adsorbent (CPC-HYDAL-MONT) is shown in Fig. 2. At 0% CPC, i. e. in HYDAL-MONT, the adsorption was extremely weak as indicated by the line along the solution concentration axis. This was in agreement with the earlier results of Pinnavaia and co-workers (8). At surfactant concentrations in excess of 12% by weight, the almost vertical nature of the sorption isotherm confirmed a strong affinity between the surface and PCP. However, these isotherms are not linear, because on an expanded scale, the plots corresponding to 12% CPC or higher showed definite tendencies towards levelling off. Our previous work on PCP adsorption on CPC-HYDAL-MONT containing 17% by weight surfactant showed that saturation adsorption was reached at much higher initial PCP concentrations than the ones used in this study (6). A comparison between CPC-MONT and a few preparations of CPC-HYDAL-MONT was undertaken, and it was observed that the adsorption isotherm for CPC-MONT was bounded by CPC-HYDAL-MONT samples having 5.5% and 14.5% by weight surfactant respectively. These results confirmed an important concept advanced in our previous work: The orientation of the adsorbed organic carbon is as important as the amount adsorbed. PCP adsorption on CPC-kaolinites was undertaken to explore the above idea even further. A linearized form of Langmuir adsorption equation was used to analyze all the data obtained in this study. The intrinsic binding constant which reflects the net change in the PCP adsorption free energy was similar for all CPC-modified clays and activated carbons. However, the monolayer capacities varied from between 8.3, 250, and 500 mmol/kg for CPC-KGA1, CPC-HYDAL-MONT (containing 14 - 17% by weight CPC) and activated carbons respectively. Thus, it would appear that a fully developed surfactant structure in the form of "hemi micelles" on the external surface of the clays was responsible for the high affinity adsorption of PCP observed in this study. The monolayer capacity, on the other hand, was governed mainly by the amount of surface organic carbon. However, CPC-MONT having 23% by weight of CPC behaved as if it had an "effective" surface CPC concentration of 11%, or roughly half the actual amount. We have previously shown that CPC-MONT underwent extensive flocculation in aqueous media (5), and this, quite likely, rendered a large fraction of adsorbed surfactant inaccessible to toxic organics. It should be noted that the PCP adsorption isotherm obtained in this study for CPC-MONT was in excellent agreement with the one reported by Mortland and co-workers (9).

ADSORPTION OF B(a)P:

Adsorption of B(a)P on CPC-HYDAL-MONT and HYDAL-MONT was studied and the results were analyzed using linearized Langmuir plots of data as was done with PCP. It was observed that even with HYDAL-MONT, the sorption of B(a)P was strong, and a limiting value of sorption was attained at 6% by weight of adsorbed surfactant. The strong affinity of B(a)P for HYDAL-MONT correlated with our previous observations of the latter's high affinity for polychlorinated dioxins (3). It was suggested that the sorption of rigid, planar molecules such as dioxins on HYDAL-MONT was mediated by charge transfer type complexes between the electronegative chlorine atoms and the Lewis acid sites on HYDAL-MONT. We postulate a similar sorption mechanism for B(a)P adsorption because of its planar structure, and the aromatic ring system, which can act as a strong nucleophile.

COAL CONVERSION WASTEWATER TESTS:

The coal conversion wastewater obtained from processing Illinois 6 coal was supplied by the coal liquefaction plant in Wilsonville, Alabama. Some of the relevant properties of the wastewater were:

pH = 9.1 - 9.3; Phenolics = 192 ppm; COD < 3000 ppm; TOC = 550 ppm;

In deionized water (pH = 9.0), the two carbons had stronger affinities for PCP than CPC-HYDAL-MONT. Further, the affinity of CPC-HYDAL-MONT for PCP in deionized water did not vary with pH. However, in WASTEWATER STREAMS, CPC-HYDAL-MONT PERFORMED BETTER THAN BOTH THE ACTIVATED CARBONS. It should be noted that all the three sorbents bound PCP much more weakly than in deionized water. But, the decline in affinity was GREATER for the carbons than it was with CPC-HYDAL-MONT. Similar results for the adsorption of B(a)P from coal conversion wastewaters were obtained. It appears that the DOC in the form of humics might have been more detrimental to activated carbons than the IOC's developed by us.

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