Using Dissolved Humic Acid To Remove Hydrophobic Contaminants from Water by Complexation—Floculation Process

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Dissolved humic acid (DHA) can be used as a complexing agent to remove hydrophobic contaminants from water by complexation—floculation process. The treatment process is composed of two stages: (a) DHA is added to the contaminated water and allowed to interact (bind) with the dissolved contaminants to form DHA—contaminant complexes (complexation stage). (b) A flocculant (alum or ferric chloride) is added, resulting in precipitation and flocculation of the DHA and the associated contaminant (floculation stage). Flocculation of DHA at concentrations of 1–50 mg/L OC HA was highly efficient with both alum and ferric chloride. The removal of three polycyclic aromatic hydrocarbons (PAHs) was studied using this process. DHA—PAH complexes did not disintegrate upon addition of Al(III) or Fe(III) salts, they were efficiently removed by flocculation, and the experimental results corresponded to those predicted by computations of the bound fractions. The proposed process is effective in removing pollutants of medium to high hydrophobicity (log Kow > 4.5). It is simple, does not require special treatment facilities, can be coupled with common water treatment technology, and has a potential to be useful in cases of periodic contamination events. Additionally, the efficient removal of DHA—contaminant complexes by flocculation emphasizes the importance of enhanced coagulation, not only to reduce the formation of disinfection byproducts (DBPs), but also to remove organic micropollutants associated with dissolved organic matter.

Introduction

The control of health-related and environmentally hazardous organic micropollutants has been and continues to be a major water quality issue. Efforts are being devoted to study the fate and transport of these contaminants. Of particular interest is the development of new technologies for remediation of contaminated sites and aquifers and for the removal of those pollutants from contaminated waters.

Dissolved humic substances (DHS) have been shown to bind (complex) organic solutes via hydrophobic interactions, forming humic—contaminant complexes in the aqueous phase. These interactions increase the apparent water solubility of hydrophobic contaminants (1–3), reduce their sorption to the soil/aquifer solid phase, and therefore decrease their retardation (4–7). Regarding contaminants transport, complexation by DHS is an undesired phenomenon because as retardation is reduced the mobility of the contaminant is increased. However, this “undesired” phenomenon can become very useful for remediation and cleanup operations. The use of DHS in flushing solutions to enhance desorption of hydrophobic contaminants from sediments was suggested by several investigators (6–9). It was further suggested by Rebhun et al. (7) to remove the humic—contaminant complexes from the flushing solution by flocculation using alum or ferric salts, followed by press-filtration and incineration or disposal of the resulting precipitate.

In this paper, we propose to extend the scope of this process (beyond the treatment of “flushing solutions”) into a novel water treatment technology, using humic acid as a complexing agent to remove hydrophobic pollutants from contaminated waters. The treatment process is composed of two stages: (a) Dissolved humic acid (DHA) is added to the contaminated water and allowed to interact (bind) with the dissolved contaminants to form DHA—contaminant complexes (complexation stage). (b) A flocculant (alum or ferric chloride) is added, resulting in precipitation of the DHA and the associated contaminant (floculation stage). This process can be applied as a novel water treatment technology for the removal of various classes of hydrophobic organic priority pollutants such as PAHs, PCBs, and chloro-organocarcinogenic pesticides from drinking water and from industrial wastewater. A flow diagram of the proposed process is shown in Figure 1.

This conceptually proposed process had to be experimentally studied. Although flocculation of DHA (mostly at low concentrations typical for natural water) is a known process, the behavior of the DHA—contaminant complexes upon addition of Al(III) or Fe(III) flocculants had to be experimentally investigated to verify that the DHS—contaminant complexes can be efficiently removed in the flocculation process.

Thus, the objectives of the present study were to prove that (a) DHS—contaminant complexes do not disintegrate upon addition of Al(III) or Fe(III) in the flocculation process and (b) that flocculation is efficient for the DHA concentrations required to complex and remove contaminants of various hydrophobics. These two aspects are critical for evaluating the feasibility of using DHA to remove contaminants from water as a novel water treatment process and to facilitate the removal of DHS—contaminant complexes from flushing solutions as conceptually proposed by Rebhun et al. (7). In addition, the feasibility of removing pollutants by the complexation—floculation process will emphasize the importance of enhanced coagulation treatment, not only to reduce disinfection byproducts (DBPs) formation but also to remove health-related contaminants that may be present in waters intended for public supply.

Three different PAHs (pyrene, fluoranthene, and anthracene), which are of medium to high hydrophobicities (Table 1) were chosen to test the feasibility of the proposed process. Beside representing one of the main groups of high priority pollutants, they were selected for their fluorescence property. This allowed us to use the fluorescence quenching technique of Gauthier et al. (10) to calculate binding coefficients of the three contaminants.

Theory

Binding (complexation) of hydrophobic organic compounds to DHS was investigated and described in numerous works (3, 5, 11–14). Binding has commonly considered as a liquid—liquid partitioning process, as evident by the observed
“isotherm” linearity, the absence of competition in multi-solute systems, and the good relationships between binding coefficients ($K_{b(oc)}$) and octanol—water partition coefficient ($K_{ow}$) values.

An equilibrium binding coefficient, $K_{b(oc)}$, can be expressed as:

$$K_{b(oc)} = \frac{C_{\text{bound}}}{C_{\text{free}}[\text{OC DHS}]}$$

where $C_{\text{bound}}$ and $C_{\text{free}}$ are the concentration of the bound and unbound pollutants respectively, and [OC DHS] is the concentration of the humic substances in terms of organic carbon. The parameter $q$ (mass of bound pollutant/mass of OCDHS) can be expressed as:

$$q = \frac{C_{\text{bound}}}{[\text{OC DHS}]} = K_{b(oc)} C_{\text{free}}$$

To evaluate the fraction of the pollutant to be removed upon addition of a certain amount of OCDHS, the $K_{b(oc)}$ of the specific pollutant needs to be determined and then the percent bound (which is to be later removed by flocculation) can be predicted using eq 3 (derived from eq 1):

$$\% \text{ bound} = \frac{K_{b(oc)} [\text{OC DHS}]}{K_{b(oc)} + 1} \times 100$$

Figure 2 visualizes eq 3. For instance, adding 10 mg/L OCDHS will remove 9, 50, and 91% of pollutants with log $K_{b(oc)}$ of 4, 5, and 6, respectively. Since these plots are based on the assumption that binding is linear (a partitioning process), the fractional removal does not depend on the initial concentration of the contaminant.

For water treatment purposes, the desired fractional removal ($f$) will be based on water quality standards, and then the desired amount of OCDHS to be added will be determined using a rearranged form of eq 3:

$$\text{OC}_{\text{DHS}} = \frac{f 10^6}{K_{b(oc)} (1 - f)}$$

A good evaluation of $K_{b(oc)}$ values is needed to calculate the required amounts of DHS needed for complexation and subsequent removal of the contaminants. For fluorescent compounds such as PAHs, the fluorescence quenching technique of Gauthier et al. (10) is the simplest method and was used for preliminary evaluations of the required DHS concentrations.

Materials and Methods

**Reagents and Chemicals.** Pyrene (Aldrich, 99% pure), fluoranthene (Fluka, Buchs, Switzerland, 97% pure), and anthracene (Fluka, 99% pure) were used as received. Concentrated stock solutions were prepared in methanol (HPLC grade, Bio Lab, Israel). All PAHs analyses were made on a
fluorometer (Shimadzu RF-1501) with excitation/emission wavelengths (nm/nm) of 333/390, 281/464, and 250/380 for pyrene, fluoranthene, and anthracene, respectively.

DHA (Aldrich, sodium salt) stock solution was prepared as follows: 2.5 g of HA was dissolved in 20 mL of 1 N NaOH, then diluted in 4.5 L of deionized distilled water (dH2O), and stirred for 2 h. The pH was adjusted to 6 with 0.5 N H2SO4, the volume was adjusted to 5 L, and the solution was stirred for an additional 3 h. The solution was finally filtered through Whatman GF-A, followed by 0.45 μm (Gelman GN-6), and its OC content was determined using a TOC analyzer (Shimadzu 5000A). The DHA stock solution was adjusted to pH 6, same as the pH chosen for binding (complexation) and flocculation, to ensure well-controlled experiments with no precipitation of DHA during the complexation stage. In actual water treatment operation, much concentrated DHA stock solution will be prepared in NaOH, and the pH will be adjusted later. It has been observed that DHA solution of 150 mg/L OCa was stable at pH 6, and therefore high DHA concentrations can be applied.

Coagulants stock solutions of alum (1.84 g/L Al2(SO4)3·16H2O, Analar, England, 98% pure) and ferric chloride (1 g/L FeCl3·Riedel-deHaen, Germany, 98% pure) were prepared for flocculation experiments.

**Determination of Binding Coefficients.** Binding coefficients (Kb(oc)) were determined in batch studies using the fluorescence quenching technique of Gauthier et al. (10) with slight modifications (18). All data were corrected for fluorescence background from DHA and for the “inner filter effect” (10).

**Flocculation Experiments.** To determine the required flocculant dose to efficiently precipitate DHA of various concentrations, a series of standard jar-test experiments was performed. Solution containing the desired concentration of DHA and 0.5 mequiv/L NaHCO3 was placed in a series of 1-L beakers, and the pH was adjusted to 6. Various flocculant dose and the desired amount of base (0.1 N NaOH), to keep a pH of 6 were added during fast stirring (100 rpm, for 5 min) followed by slow stirring at 25 rpm for 25 min. The degree of clarification (total absorbance) and the concentration of residual DHA were determined with a spectrophotometer (Milton Roy, Spectronic 601) and with a TOC analyzer after overnight settling.

**Using DHA to Remove PAHs.** The mechanism of DHA–PAH complexes removal was tested in a flocculation jar test. DHA (16.5 mg/L OCa) was added to a pyrene solution, stirred for 5 h (to approach binding equilibrium; 18), and then various amounts of alum were added to a series of beakers until efficient flocculation of the DHA was achieved. The remaining DHA and pyrene in the supernatant were determined after overnight settling on a spectrometer and fluorometer, respectively. At low dosage of alum, where only some of the DHA was removed, it was not possible to simply record the fluorescence intensity of the PAH in the aqueous supernatant since some of it was bound to the DHA that remained in the supernatant. Therefore, pyrene was extracted from the supernatant with hexane by transferring 5 mL of the aqueous phase and 5 mL of hexane (Uvso, Merck, Darmstadt, Germany) into a tube, shaking gently 50 times by hand, and then recording the fluorescence in the hexane phase. In a preliminary analysis, it was found that extraction efficiency was at least 98% in the absence of DHA but decreased to about 80% with the presence of 16 mg L OCa. Therefore, extraction efficiency was plotted against various OCa concentrations, and the fluorescence values were corrected according to that curve.

Removal of PAHs was tested for various DHA concentrations (5, 16.5, 30, and 50 mg/L OCa), expecting to remove a wide range of fractions of the three contaminants. DHA was added to the solution containing the PAH and allowed to interact, while stirring, for 5 h. Then flocculation was performed with alum or ferric chloride in the same manner as described before. The PAHs that remained in the clarified solution were determined using a fluorometer. Hexane extraction was not required in these experiments since the DHA was efficiently removed and the fluorescence intensity of the aqueous supernatant could be simply recorded. Although flocculation was highly efficient (see results), fluorescence data were still corrected for the inner filter effect and fluorescence background from DHA residues (10).

**Results and Discussion**

**Binding of PAHs to Dissolved HA.** The binding coefficients obtained by the fluorescence quenching technique are summarized in Table 2. These values were initially used to evaluate the amounts of OCa needed to obtain various degrees of removal of the three PAHs using eq 4. The OCa concentrations that were chosen to be tested in this study (5–50 mg/L) were expected to remove up to 86, 85, and 73% of pyrene, fluoranthene, and anthracene, respectively.

**Flocculation of DHA.** The results for 16.5, 30, and 50 mg/L OCa are represented in Figure 3 for alum (a) and for ferric chloride (b). Flocculation with both flocculants was successful at all OCa concentrations with up to 98% reduction in the total absorbance and up to 96% TOC removal (not shown). The increase in absorbance at low flocculant dose resulted from light scattering by small, nonsettleable Me(III)–HA precipitates.

Humic substances, being anionic polyelectrolytes, can react chemically with Al(III) or Fe(III) salts, forming Me(III)–HA precipitates. At an appropriate Me(III) to humic ratio, the negative charge of the humic molecule is neutralized and settleable flocs are produced. Depending on the pH and Me(III) dose, the concentration of the latter may exceed its solubility, resulting in the formation of solid-phase hydroxide precipitate (Me(OH)2(s)). Free HA or Me(III)–HA complexes may adsorb to the Me(OH)2 precipitates and at higher doses may be enmeshed in a sweep floc. Sweep floc occurs when the concentration of alum or ferric salt is sufficiently high to cause rapid precipitation of metal hydroxide, and colloidal particles are enmeshed in the precipitates as they are formed. In a real situation, a continuum of the above reaction mechanisms may take place (19–22). As seen in Figure 3, flocculation continued to be highly efficient at very high flocculant doses, indicating that the first reaction stage, either Me(III)–HA precipitate formation or adsorption of free HA on solid Me(III) precipitate, was followed by a sweep floc stage.

The relationships between OCa concentration and the required flocculant dose are presented in Figure 4. Different stoichiometric relationships seem to exist for low and high OCa concentrations. Stoichiometric relationships, as observed in other works (20, 23–24), indicated that flocculation was achieved by charge neutralization mechanism. Similar to the results of this study, Narkis and Rehmun (20) found a deviation from linear stoichiometry at high concentrations of HA and FA. Nonlinear stoichiometry was suggested to be an indication to the mechanism of humic adsorption on Al(OH)3(s) precipitate (24). Figure 4 suggests that a transition

| Table 2. Kb(oc) Values Obtained by the Fluorescence Quenching Method and the Amount of OCa Needed to Obtain 50 and 90% Removal |
|-----------------|----------|----------|
| PAH             | log Kb(oc) (mL/g) | OCa (mg/L) |
| pyrene          | 5.08     | 8        | 9        |
| fluoranthene    | 5.06     | 9        | 78       |
| anthracene      | 4.74     | 18       | 163      |
from charge neutralization as a governing mechanism (low OCHA concentration) to adsorption mechanism (high concentration) may exist.

**Removal of PAHs by Complexation–Flocculation Process.** A preliminary study showed that PAHs are not adsorbed to alum flocs in the absence of DHA in the flocculation process (18).

The removal of PAH–DHS complexes was studied in flocculation jar tests using various alum doses (Figure 5). It is seen that the removal efficiency of pyrene followed the removal efficiency of DHA. At the required alum dose, flocculation of DHA was highly efficient (low absorbance), and high removals of pyrene were obtained. This figure elucidates two critical points regarding the mechanism of DHA–PAH complexes removal: (a) The removal of PAH is facilitated via DHA–PAH complexation followed by an efficient flocculation. (b) DHA–PAH complexes do not disintegrate upon the addition of Al(III) and Fe(III) salt in the flocculation process.

Other PAH removal experiments were performed with alum or ferric chloride at various OCHA concentrations using the flocculant dose required to achieve efficient DHA removal. Figure 6 summarizes the experimentally obtained removals of pyrene (a), fluoranthene (b), and anthracene (c) using 5–50 mg/L OCHA. For each of the PAHs, the predicted percent removal was plotted (solid lines) based on the $K_{boc}$ as determined by the fluorescence quenching technique (Table 2) using eq 3. For pyrene and fluoranthene, the experimental and predicted results were very close. For anthracene, the experimental results were somewhat lower than those calculated.

The complexation–flocculation process is effective only if the PAH–DHA complexes are stable and do not disintegrate in the flocculation process. The bonding stability of the complexes is evident from Figure 5 and particularly by the excellent correspondence of predicted and experimental results (Figure 6a,b). Flocculation of DHA is facilitated via acidic hydrophilic sites (carboxylic and phenolic groups) on the humic molecule that are likely to react with the positively charged hydrolys species of Al(III) and Fe(III). On the other hand, hydrophobic sites on both aliphatic and especially aromatic constituents of the humic molecule are responsible for the association between humics and nonionic molecules.
(such as PAHs and other hydrophobic compounds). Since Al(III) or Fe(III) and the pollutant each react with different sites on the humic material, a competition between them is not expected. The bound compound in the DHA—PAH complex is precipitated, flocculated, and entrapped in aluminum or ferric flocs in the same way and extent as the DHA itself. The observation that anthracene removal, based on the \( K_{b(oc)} \) obtained by fluorescence measurements, was lower than expected had initiated a detailed work that compared the \( K_{b(oc)} \) values obtained by the fluorescence quenching technique and by the complexation—flocculation process (18). It was concluded that removal by flocculation is actually a very promising method to analyze \( K_{b(oc)} \) values. The fluorescence quenching technique, although elegant and widely used, may overestimate \( K_{b(oc)} \) values because of experimental artifacts (16, 17).

**Applications and Advantages of the Complexation—Flocculation Technology.** DHA can be easily produced by extraction from peat or lignite (both rich in humic acid and abundantly available in most countries) with sodium hydroxide and removal of the undissolved residue by settling and/or filtration. A concentrated solution of DHA in NaOH will be supplied from production facilities to water treatment plants.

The complexation—flocculation process can be applied as a novel water treatment technology to remove contaminants from drinking water. The success of removing DHA—contaminant complexes by flocculation is also important for facilitating the use of DHA in soils and aquifers flushing. This novel technology may also be used to reduce the toxicity of complex industrial wastewater, similar to the use of powder-activated carbon (PAC).

This technology is applicable for relatively highly hydrophobic compounds. The percent of contaminant removal was calculated for the range of \( \log K_{b(oc)} \) of 2–7, with applications of 50, 100, and 150 mg/L OC HA. The predicted percent removals are represented in Figure 7. Effective removal of at least 50% of the contaminant is expected for pollutants with \( \log K_{b(oc)} > 4.5 \). Among these compounds are various priority pollutants such as PAHs (e.g., pyrene, fluoranthene, benzo(a)pyrene, perylene), PCBs (tetra-, pentachlorobiphenyls), and chloro-organic pesticides such as DDT. Using reasonable flocculant dose, the proposed technology has a potential to reduce many contaminants levels below drinking water standards. For example, if pyrene

![FIGURE 6. Percent removal of pyrene (a), fluoranthene (b), and anthracene (c) by various concentrations of OCHA. Flocculation was achieved with alum (■) or with ferric chloride (○). Solid lines represents the expected removal based on the binding coefficients obtained by the fluorescence quenching technique.](image)

![FIGURE 7. Expected percent removal of a pollutant with \( \log K_{b(oc)} \) of 2–7 using 50, 100, and 150 mg/L OC HA.](image)
(log $K_{oc}$ = 5) is found in a concentration of 0.3 µg/L, then 10 mg/L ODAH and about 25 mg/L alum (as aluminum sulfate) will be required to reduce its concentration to 0.15 µg/L, which is below the SDWA drinking water standards (29).

A major advantage of this technology is that, similar to the use of PAC, it is simple and does not require investment in special facilities. It is therefore suitable to be used periodically for abrupt periodic contamination events. This is in contrast to the use of granular activated carbon (GAC), which requires special facilities and is not cost-effective to use on a periodic basis. For example, PAHs levels in urban runoff (30) were usually low in the range of nanograms per liter. However, fluoranthene (log $K_{oc}$ = 5) was detected in levels as high as 8.1 µg/L. This periodic contamination could be treated with DHA; addition of 90 mg/L ODAH could reduce its concentration by 90% (eq 4).

Additionally, it is an advantage that this technology is coupled with the general water treatment process. Flocculation process is usually an integral part of water treatment, aimed at removing organic and inorganic colloids and dissolved organic matter (DOM). Adding more DHA as a part of the treatment process will only require higher flocculant dose, but the treatment process will essentially remain the same.

The success of contaminants removal via the complexation–flocculation process further emphasizes the importance of enhanced coagulation treatment. Enhanced coagulation is usually designed to remove more efficiently DOM (especially DHS) to reduce the formation of disinfection byproducts (DBPs), which are of detrimental health effect. It is evident from this study that enhanced treatment is important also to remove micropollutants that are associated with DHS or with humic-coated inorganic colloids.

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Literature Cited


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