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Immobilized humic substances as sorbents

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Abstract

A new method was developed for the immobilization of humic substances. Humic acids (HA) immobilized onto different carriers were studied as sorbents for organic and inorganic substances. The sorption isotherms of 4-aminoazobenzene, Crystal Violet, Methylene Green, and flavine mononucleotide on immobilized HA show that pH and salt concentration have a significant effect on the sorption process, largely depending on the properties of polymeric matrix. Humic acids from different sources showed differing sorption capacity for the studied groups of substances.

Keywords: Humic acids; Sorbents; Immobilization

1. Introduction

Humic substances (HS) play a major role in the biogeochemical cycling of carbon and they are major organic substances in soils and waters, thus being of importance also in fossil organic deposits, especially peat and low rank coal (MacCarthy, 2001). Due to their multifunctional character (presence of numerous carboxylic and phenolic, but also keto-, and aminogroups) humic substances are able to complex heavy metals and persistent organic xenobiotics (Leenheer et al., 2003). Many important processes in the environment are influenced through interaction with humic substances, for example with solid phases in soils and natural waters. At the interactions both organic (usually detritus particles) and inorganic (mineral matter) substances become covered with humic substances and thus contaminant movement can be largely modified by interaction with humic substances (De Paolis and Kukkonen, 1997). Interaction of humic substances with xenobiotics can modify the uptake and toxicity of these compounds and affect the fate of pollutants in the environment. The properties and the structure of the HS depend on their origin (Ritchie and Perdue, 2003).

To offer new areas of use and to study the interaction between xenobiotics and humic substances, their immobilization on solid carriers (Bulman and Szabo, 1991; Klavins, 1993; Klavins and Eglite, 2000) has been suggested. Considering the wide application of immobilized enzymes and low molecular biologically active molecules in chromatography and biotechnology, immobilization of HS has received substantial interest. Several approaches for immobilization of HS have been suggested. Immobilized HS were used to study the interactions of HS with metal ions and organic substances (Koopal et al., 1998; Yang and Koopal, 1999; Laor et al., 2002; de la Rosa et al., 2003; Prado et al., 2003), and as models

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of humate-coated minerals to study migration of ^{241}Am around nuclear waste repositories (Szabo et al., 1998).

Considering immobilized HS as prospective sorbents for organic and inorganic substances, the aim of the present study is to study the sorption character of organic substances and metal ions onto humic substances isolated from different environments and immobilized onto differing polymeric matrixes.

2. Materials and methods

The properties of commercial humic acid (Aldrich Chemical Co. Ltd.) and obtained humic acids isolated from soil, peat and water as are described earlier (Klavins and Eglite, 2000). Elemental analysis was carried out by a Perkin–Elmer 240B analyzer.

The specific surface areas of the prepared solid phases were determined by the Brunauer–Emmet–Teller (BET) method using a EMS-61 Sorptometer. Adsorption isotherms of N_2 were determined volumetrically at 100 °C. Prior to the measurements each sample was dried in vacuum at 383 K for 1 h. The maximum error in these measurements was about 5%.

Humic substances were immobilized as described earlier (Klavins and Eglite, 2000) and their basic properties are summarized in Table 1.

Adsorption of *p*-aminoazobenzene (4-amino-1,1′-azobenzene, *p*-AAB) on immobilized humic acids was conducted as batch experiments in 100 ml sealed glass bottles on a rotary shaker table 24 h at 20 °C. 30 ml of either 10, 30, 50, 70, 90, 120 mg l^{-1} solutions of *p*-aminoazobenzene with 100 mg of sorbent were shaken until equilibrium was reached (24 h). After separation of the phases by filtration through Watman paper filter, the concentrations of *p*-AAB in the supernatant phase were determined spectrophotometrically (using a HACH 2000, glass cell with path length 2.5 cm) as absorption at 470 nm (values obtained from initially prepared calibration graph). The quantity of *p*-AAB adsorbed to different phases was determined from the difference of the initial aqueous phase concentration and the amount in solution at equilibrium. Sorption of Crystal Violet (CrV), Methylene Green (MethG), flavine mononucleotide (FMN) and metal ions on immobilized humic substances was performed similarly. Concentrations of metal ions were determined using atomic absorption spectrometry in an air–acetylene flame (Perkin–Elmer 2380 with double beam and deuterium background corrector). pH of solution has been adjusted using citric acid—phosphate buffers.

The sorption test was performed in a laboratory scale column (10 × 250 mm) filled with humic acid immobilized onto aminopropylsilica (IV). A *p*-AAB solution (1; 2; 3 mg l^{-1}) was percolated through the column with a velocity 6 ml min^{-1}, sampling fractions of 18 ml with a "Pharmacia Fine Chemicals" fraction collector and analyzing concentrations of the humic acids remaining in solution.

3. Results and discussion

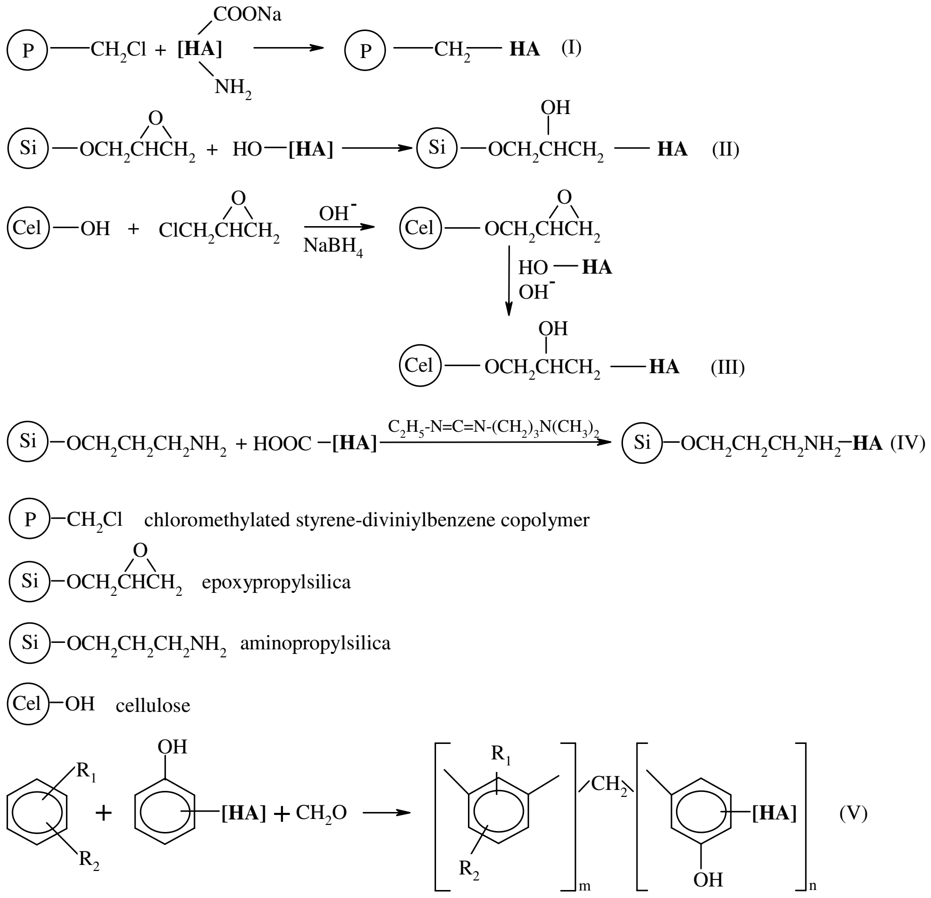
Considering that the properties of humic substances depend on their origin, humic acids of commercial origin (HA_C) as well as HA isolated from the major sources, soil (HA_S) and peat (HA_P), were used to cover the variability in properties of humic acids.

The following methods (Klavins and Eglite, 2000) have previously been used for the immobilization of HS (Fig. 1):

(I) Immobilization by grafting on Merrifield resin or chloromethylated macroreticular styrene–divinylbenzene copolymer;
(II) Immobilization on epoxypropylsilica;

Table 1
Properties of immobilized humic acids

Immobilized HA	C (%)	H (%)	N (%)	COOH (mmol g^{-1})	Content of HA (mg g^{-1})	Swelling with water (ml g^{-1})	Swelling with benzene (ml g^{-1})
I-HA_C	86.17	7.29	0.21	0.185	120	0.87	1.85
I-HA_S	76.12	9.16	0.97	0.153	228	0.59	1.06
I-HA_P	77.03	8.21	0.43	0.131	208	0.48	1.01
II-HA_C	12.32	3.74	0.12	0.072	57	0.11	0.35
II-HA_S	12.31	4.76	0.32	0.065	85	0.12	0.45
III-HA_S	43.86	7.30	1.50	0.098	83	0.18	0.56
III-HA_C	42.20	6.13	0.30	0.86	87	0.22	0.64
IV-HA_C	4.67	0.59	0.31	–	7	0.12	0.12
V_A–HA_C	53.93	3.59	1.33	0.723	373	1.15	2.35
V_B–HA_C	66.24	6.39	0.05	1.180	340	0.73	1.87
V_C–HA_C	58.60	6.51	0.13	0.943	185	0.82	1.84
V_D–HA_C	60.98	6.30	0.78	1.322	430	1.14	2.40



R$_1$, R$_2$ - H;OH; CH$_3$
V$_A$ - polycondensation of humic acid
V$_B$ - R$_1$=H, R$_2$=OH
V$_C$ - R$_1$=H, R$_2$=CH$_3$
V$_D$ - R$_1$, R$_2$=OH

Fig. 1. Methods used for immobilization of humic substances: (I) by grafting on Merrifield resin; (II) on epoxypropylsilica; (III) on epoxypropycellulose; (IV) on aminopropylsilica; (V) by polycondensation with formaldehyde (V_A); phenol (V_B); toluene (V_C) and resorcinol (V_D).

(III) Immobilization on epoxypropycellulose;
(IV) Immobilization on aminopropylsilica using coupling by means of water soluble carbodimide;
(V) Polycondensation of HA with formaldehyde and molecules able to enter in condensation reactions (phenols).

The suggested approaches allow to remove the immobilized humic macromolecule from the surface of polymer chain and to increase the flexibility of interactions of immobilized humic substances with sorbates.

The obtained immobilized HS were characterized by elemental and functional analysis, as well as by the amount of immobilized HS (Table 1). The differing matrices used in the study and the variability of humic substances employed allow to obtain a range of sorbents with different hydrophobicity of the polymeric matrix, concentration of immobilized humic substances, and also porosity. The surface area of polymers obtained using polycondensation (V_A–V_D, Fig. 1) is low (0.326–0.580 $m^2\ g^{-1}$), higher for sorbents (I) on macroreticular styrene–divinylbenzene copolymer (51.6 $m^2\ g^{-1}$), and

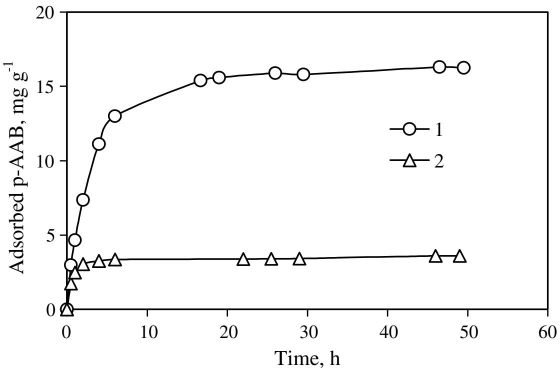


Fig. 2. Sorption kinetics of *p*-aminoazobenzene (*p*-AAB) on immobilized humic acids: (1) I-HA_S, (2) IV-HA_C.

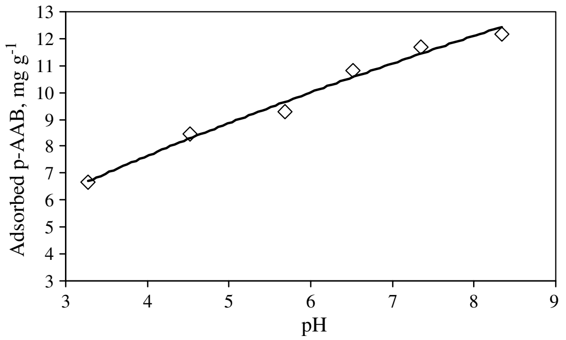


Fig. 4. Sorption of *p*-aminoazobenzene on immobilized humic substances V_B–HA_{coal} (size of polymer particles 0.063–0.160 mm) depending on the pH of the solution.

for sorbents on silica (II, IV) it can reach even $106\ m^2\ g^{-1}$.

The sorption kinetics (Fig. 2) on the immobilized humic acids depends on porosity of the polymeric matrix and the hydrophilicity/hydrophobicity balance of the sorbates, being fast for sorption on macroreticular polymers, but comparatively slow on gel-type polymers (immobilized humic substances on styrene–divinylbenzene copolymers or polycondensation polymers).

The character of the sorption process depends on the salt concentration in the solution (Fig. 3). Also in this case the sorption capacity depends on the porosity of the polymer structure which is insignificant for gel-type polymers and substantial for sorbents on aminopropylsilica. The *p*-AAB sorption ability on immobilized humic substances depends also from pH, and with increase of pH in the solution the sorption capacity is increasing (Fig. 4).

The sorption isotherms of *p*-aminoazobenzene (*p*-AAB) on immobilized humic substances are shown in Fig. 5. The adsorption of *p*-aminoazobenzene on immobilized humic substances differs substantially depending on the properties of the original polymeric carrier. On silica polymers the sorption capacity is low (Yang and Koopal, 1999), while on humic substances immobilized on Merrifield resin it can be quite high. However, for polymers obtained using polycondensation with formaldehyde, the specific polymeric matrix as such does not exist. To compare the obtained immobilized humic substances, the sorption was expressed as mg of *p*-AAB on 1 g of sorbent. The experimental data were fitted to empirical Freundlich and Langmuir adsorption equations. We found that the Langmuir isotherm gave the best fit for the description of the *p*-aminoazobenzene sorption. The r^2 values together with Langmuir empirical constants are given in Table 2. Comparison of adsorption isotherms shows substantial differences between the obtained polymers and, possibly also the major impact of the original polymeric matrix: for polymer obtained by grafting humic acid onto Merrifield resin the sorption capacity is higher and can be described by

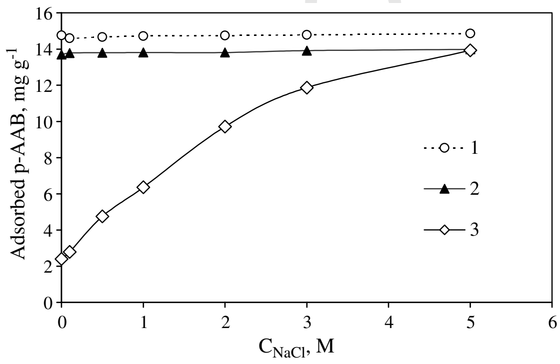


Fig. 3. Sorption of *p*-aminoazobenzene on immobilized humic acids: (1) V_C–HA_P, (2) I-HA_S, (3) IV-HA_C depending on the ionic strength of the solution.

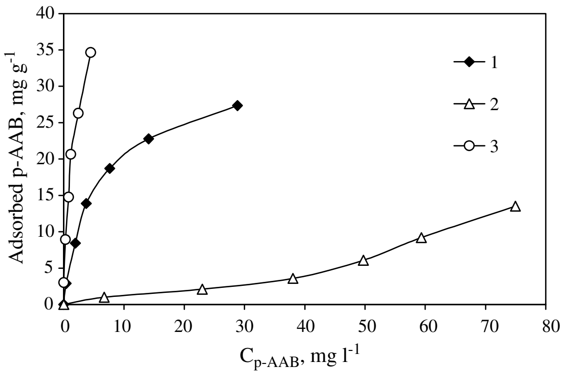


Fig. 5. Sorption of *p*-aminoazobenzene on immobilized humic acids: (1) I-HA_S, (2) IV-HA_C, (3) V_C–HA_P depending on the type of polymeric matrix.

Table 2
Langmuir constants (K and b are empirical constants related to bonding energy and sorption maximum, respectively) for the sorption of *p*-aminoazobenzene on immobilized humic acids

Immobilized HA	K	b	r^2
I-HA_S	3.226	0.066	0.88
II-HA_C	0.021	0.01	0.91
III-HA_S	0.085	0.018	0.94
IV-HA_C	0.043	0.031	0.98
V_A–HA_C	0.121	0.039	0.99
V_C–HA_C	6.599	0.055	0.95
V_D–HA_C	0.024	0.028	0.97

the Langmuir model, while the sorption capacity on humic substances immobilized onto silica is lower. The Langmuir constants K and b, indicating bonding energy and the maximum sorption capacity, respectively differed from sample to sample, suggesting that various mechanisms of sorption may occur.

The sorption on HS immobilized on a carrier especially on a polymer carrier obtained using polycondensation much depends on the size of the polymeric particles (Fig. 6). The sorption takes place faster for small polymer particles and follows the Langmuir model. However, on large polymer particles obtained using polycondensation (V_A–V_D, Fig. 1), the sorption follows the so-called S-type form, indicating a low surface affinity that increases with surface saturation with sorbate. The polycondensation polymers are gel-type, their swelling in aquatic media much depends on the polymer composition, the sorption in this case is evidently lower than on macroreticular polymers, it takes place on the surface layers of sorbent, and it is diffusion controlled.

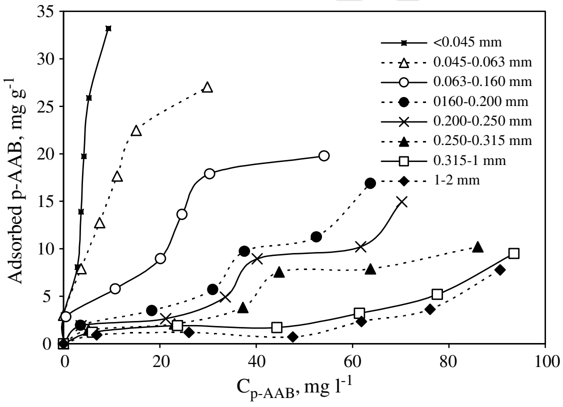


Fig. 6. Sorption of *p*-aminoazobenzene on immobilized humic substances V_B–HA_{coal} depending on the size of polymer particles.

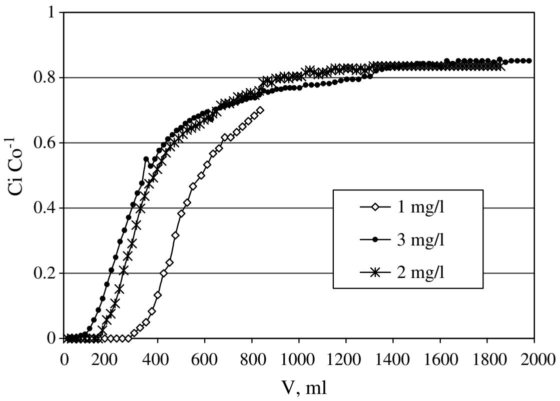


Fig. 7. Sorption of *p*-aminoazobenzene on humic acid immobilized on aminopropylsilica (IV-HA_C) in a laboratory scale column.

The obtained immobilized humic acids demonstrated good sorption properties for column processes (after Fig. 7). For column processes, the most effective sorbents are obtained using more rigid matrices (silica, crosslinked styrene–divinylbenzene copolymer with a high degree of crosslinking) and the retention processes much depend on the concentration of sorbate.

In comparison to the sorption process of *p*-aminoazobenzene, the character of sorption differs for higher molecular-weight polar sorbates, such as the dyes Crystal Violet, Methylene Green, and flavine mononucleotide (Fig. 8). All of these isotherms clearly exhibited evidence for a sequence of adsorption steps and a relatively low affinity of immobilized humic substances with respect to hydrophilic cationic sorbates.

The first stage of the adsorption is characterized by relatively low sorption efficiency, but is followed with a significant increase of the sorbed amount. The affinity of selected sorbates towards the sorbent significantly increases after surface saturation of sorbents is reached. However, immobilized humic substances cannot be considered as good sorbent for sorption of hydrophilic cationic sorbates.

As it is well known, humic substances in solution can form stable complexes with metal ions as well as with organic molecules (after Fig. 8). The same is true also for immobilized humic substances, as shown by the observed sorption of some metal ions and some organic substances (Table 3). Immobilized HS have rather good sorption capacity for a wide range of substances. They are prospective for the investigation of humus properties and can serve as a potential inexpensive sorbents for removal of metal ions and both hydrophobic and hydrophilic organic substances during waste water treatment and drinking water purification procedures.

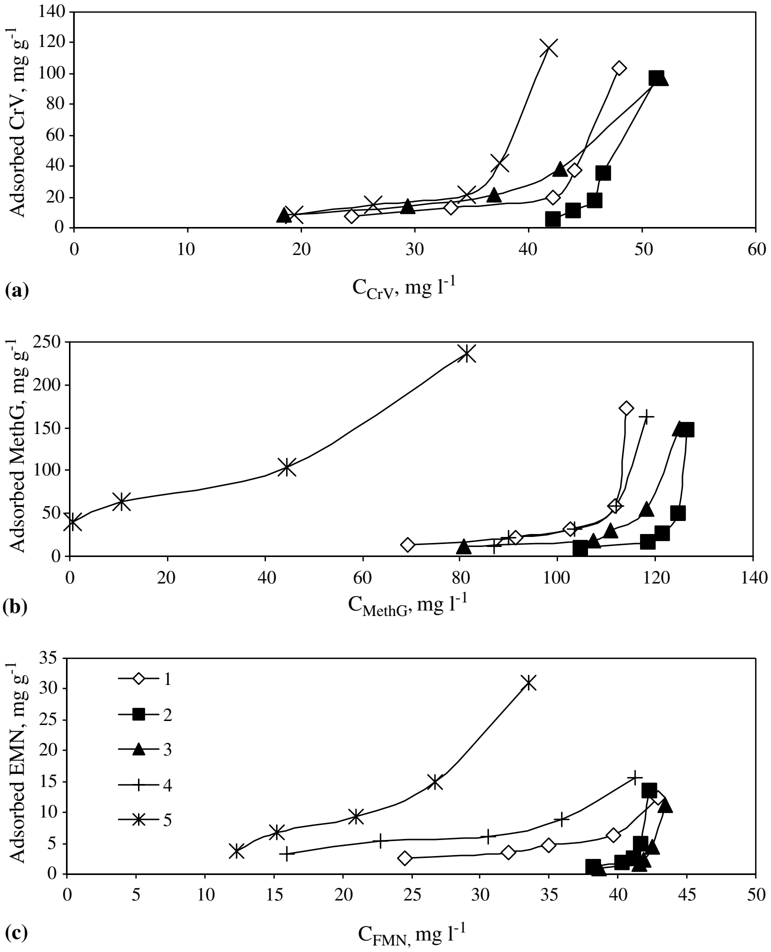


Fig. 8. Sorption of (a) Crystal Violet (CrV), (b) MethyleneGreen (MethG) and (c) flavine mononucleotide (FMN) on immobilized humic acids: (1) I-HA$_S$, (2) V_B–HA$_P$, (3) III-HA$_C$, (4) IV-HA$_C$, (5) V_C–HA$_P$ depending on the type of polymeric matrix.

Table 3
Sorption of metal ions and organic molecules on immobilized humic substances

IM HV	Cu^{2+} (mg g^{-1})	Co^{2+} (mg g^{-1})	Ni^{2+} (mg g^{-1})	Mn^{2+} (mg g^{-1})	Cd^{2+} (mg g^{-1})
I-HA$_C$	2.5	1.3	1.3	2.4	9.0
I-HA$_P$	10.6	2.8	1.7	3.7	0.0
II-HA$_S$	2.5	1.6	0.3	1.9	9.0
III-HA$_C$	4.6	2.3	1.6	2.7	9.5
IV-HA$_C$	11.9	9.8	5.9	10.1	19.8
V_A–HA$_C$	2.2	1.9	1.3	1.8	9.0
V_B–HA$_C$	6.9	3.6	2.3	3.3	11.0
V_C–HA$_C$	3.1	1.7	1.1	2.8	7.3
V_D–HA$_C$	4.3	1.9	1.7	5.7	13.5

4. Uncited references

Diallo et al. (2003), Senesi et al. (1989), Senesi and Sakallariadou (1994), Thurman (1985), Thurman and Malcolm (1981), Weber and Huang, 2003.

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