Designing Core–Shell Materials Using Humic Acids

T S Skripkina, E M Podgornuskikh and O I Lomovsky

Institute of Solid State Chemistry and Mechanochemistry SB RAS, Novosibirsk, 630128, Russia

Abstract. Due to the high content of complexing moieties, humic acids are promising compounds for designing heavy metal sorbents that can be used in natural environment objects. Experiments focused on designing sorbent particles containing a humic shell and a core (that is supposed to impart the desired performance characteristics to the particle) and applying humic acids onto various materials were conducted. It is demonstrated that the sorbent with a “lignocellulosic core–humic shell” structure can be produced mechanochemically. The efficiency of humic acid binding to lignocellulosic materials directly correlates with lignin content within lignocellulosic materials. A method for passing lignin from the surface of lignocellulosic biomass into the solution using humic acids is found. Unmodified highly lignified biomass is the optimal material for applying humic acids onto lignocellulosic materials.

1. Introduction
The interactions between humic acids and various materials are now being actively studied around the globe with different purposes. The sorption of humic acids onto such materials as nanosized zero-valent iron [1], nanosized inorganic oxides [2], graphene oxides [3], argillaceous minerals [4], chitosan granules [5], and polyacrylonitrile fibers [6] has been investigated. Humic acids are able to immobilize heavy metals partially due to precipitation of humic acid–metal complexes onto the fixed phase (argillaceous minerals, metal oxides, or silicates present in soils or bottom sediments [7]).

Among inorganic materials, carbon-based sorbents and silica gel varieties characterized by high surface area are also commonly used. Silica gel is subjected to pretreatment (typically with organosilanes). This process is conducted using organic solvents in anhydrous media at elevated temperatures. The data on sorption of humic molecules onto organic compounds or natural materials are very scarce because the analyzed system is very complex and there exist methodological challenges. However, it is widely recognized that the problem of searching for an abundant natural material that can adsorb humic acids is relevant today as these materials reduce the environmental load. Functional trimethylammonium-modified cellulose nanofibers were shown to efficiently bind humic acids. However, although this material is based on cellulose, it is a product of sophisticated multi-step synthesis [8]. Chitosan supported onto a clay substrate is another natural polymer for which the kinetic parameters and the mechanism of binding to humic acids have been studied [9].

It is reasonable to investigate the humic acid binding ability for a range of lignocellulosic materials of different chemical compositions (from isolated lignin and cellulose to lignocellulose varied different degree of chemical modification). Lignin is known to constitute up to 44% of peat and soil humic substances. The high affinity of humic acids for lignin is also attributed to the fact that these substances carry moieties of similar nature (mainly the orthophenolic ones). In addition to studying plant-derived materials having a natural structure, it is interesting to investigate the ability of lignocellulosic biomass with a modified structure to bind humic substances. Earlier, E.M.
Podgorbunskikh et al. [10] developed a method for increasing lignin content on the particle surface by mechanochemical pretreatment of the material in a laboratory-scale mechanochemical activator (attritor) at a temperature of lignin devitrification [10]. Under these pretreatment conditions, plant biomass lignin undergoes a phase transition to a rubber-like state, leaves the cell wall and is accumulated on the surface of the nascent particles. High lignin content on the surface of plant biomass, in combination with significant porosity, can impart an enhanced sorption capacity with respect to humic acids to the biomass. Verification of this hypothesis will substantially contribute to the development of complex sorbents based on humic acids.

The objective of this study was to design complex heavy metal sorbents with a core–shell structure.

2. Materials and Methods
A number of materials, both inorganic and organic, were selected for the experiments focused on supporting humic acids onto sorbents. The inorganic materials included activated carbon, mesoporous carbon adsorbent (MC), silica gel powder, and silica gel granules. Organic substrates were represented by a range of lignocellulosic materials of different chemical composition and morphology, including isolated lignin and cellulose, partially delignified wheat straw, lignocellulose after water extraction, and rice husk. The sorption of humic acids onto highly lignified materials (mechanically modified reed biomass and wheat straw) was also studied.

Humic acids manufactured by Aldrich were used in the experiments. The content of humic acids in the solution was determined spectrophotometrically on an Unico 2800 spectrophotometer (USA) at 465 nm in polystyrene cells with respect to water. Prior to each analysis, calibration curves were plotted using the points corresponding to humic acid concentrations of 250, 150, 100, 50, and 10 mg/l. The samples were preliminarily centrifuged and filtered using red ribbon filter paper.

The specific surface area (Ssp) of the test samples was measured using the nitrogen desorption method on a Sorbtometr-M instrument; the data were analyzed using the Bruner–Emmett–Teller (BET) equation. The morphology of the materials was studied by scanning electron microscopy on a Hitachi TM-1000 microscope and gold pre-deposition onto the surface (sputtering time, 1 min; ionic current, 30 mA). The composition of lignocellulosic materials was analyzed by successive extraction with hexane, ethanol, and water, followed by acid hydrolysis and delignification. The yields of the extracts were determined according to weight loss.

Sorption of Humic Acids onto Various Materials. One gram of each material was added to 50 ml of humic acid solution (250 mg/l, pH 7.0). The resulting suspension was thermostated at 25°C and shaken at a frequency of 130 min−1. Samples were taken at the initial instant and 48 h later to determine the content of humic acids remaining in the solution.

Desorption of Humic Acids. The materials with adsorbed humic acids were placed in a test tube containing 20 ml of Tris–HCl buffer (pH 9.0). The resulting suspension was thermostated at 25°C and shaken at a frequency of 120 min−1. After 5 h, solution samples were taken to determine the content of desorbed humic acids.

3. Results and Discussion
The chemical compositions of the materials used in this study as the “core” to support humic acids were preliminarily determined.

Water content in the materials was as follows: activated carbon, 3.5 ± 0.2 %; MC, 2.3 ± 0.1%; silica gel granules, 5.0 ± 0.2 %; and silica gel powder, 4.4 ± 0.2%. The series of plant-derived materials for supporting humic acids was originally selected so that the contents of the key components (lignin, cellulose, and hemicelluloses) were maximally diverse [11]. Lignin content was the highest for hydrolysis lignin (80.0 ± 0.9 %) and the lowest for microcrystalline cellulose (< 0.05%) and delignified wheat straw (3.0 ± 0.1 %). That is the key difference between delignified wheat straw and lignocellulose after water extraction, which has a similar composition. Cellulose content is minimal for hydrolysis lignin and maximal for microcrystalline cellulose and delignified wheat straw (89.0 ± 0.9 %), being slightly lower for lignocellulose after water extraction (74.0 ± 1.0 %).

The inorganic materials have similar morphology and differ only in terms of their particle size and ability to form agglomerates.
A morphological analysis of plant-derived materials demonstrated that they have a complex multi-level architecture, except for isolated lignin and microcrystalline cellulose. Lignin is a finely dispersed powder. The cellulose morphology is represented by fibrous fragments composed of fibrils up to 500 µm long and 10–20 µm wide. The morphology of delignified wheat straw is represented by fibers resembling those in the initial wheat straw and regions of the cross-linked structure with a large number of pores. The fibers are loosely packed and oriented parallel to each other so that particles have many large voids. The morphology of lignocellulose after water extraction is similar to that of delignified wheat straw but has higher pore content. Both samples have a well-defined pore structure (pore size, 3–6 µm). This happens because the rigid cellular framework starts to have vacancies as some soluble substances are dissolved, so humic substances can be bound via the mechanism of physical sorption.

Rice husk has an interesting morphology as its structure is rather complex. The outer side of the particles is covered by a cellulose silica membrane. The inner side consists of lignocellulose and has a smooth surface. Rice husk is a unique material due to its silicon dioxide content, which is extremely high for plant biomass, and exists in the amorphous form on the material surface. Silicon dioxide is accumulated near the outer surfaces of the plant tissue to form the cellulose silica membrane [12].

Table 1 shows the results of experiments on sorption/desorption of humic acids on inorganic materials.

Table 1. Parameters of sorption of humic acids onto inorganic materials and specific surface area values for the materials constituting the “core”

| Material            | Sorption (mg/g) | Desorption (mg/g) | Sorption capacity (mg/g) | Relative sorption capacity (mg/m²) | S_{sp} (m²/g) |
|---------------------|----------------|-------------------|--------------------------|-----------------------------------|--------------|
| Silica gel powder   | 6.3            | 1.7               | 4.6                      | 0.014                             | 309 ± 9      |
| Silica gel granules | 5.7            | 0.83              | 4.9                      | 0.02                              | 207 ± 7      |
| Activated charcoal  | 6.9            | 0.00              | 6.9                      | 0.02                              | 280 ± 9      |
| MC                  | 13             | 0.25              | 13                       | 0.04                              | 350 ± 10     |

Carbon-based materials exhibited better sorption properties with respect to humic acids than silica gels did. The modified nano-carbon sorbent can remove the greatest amount of humic acids from the solution due to the lower size of its particles and higher surface area compared to the regular activated charcoal. Silica gel granules exhibited worse sorption properties than silica gel powder because silica gel particles had a higher specific surface area.

Simultaneously with being more efficient in removing humic acids from the solution, carbon-based materials showed better ability to retain humic acids. It should be mentioned that the degree of desorption from the surface of silica gel powder was the highest, which can be attributed to low porosity of this material. The desorption degree does not make any significant contribution to choosing the material for the “core.” With allowance for the inaccuracy, the sorption capacities of silica gel granules and powder were equal; the maximum sorption capacity was observed for the modified nano-carbon sorbent.

Hence, among inorganic materials, carbon-based sorbents showed better results than silica gel did. One should take into account that activated charcoal is a much more accessible feedstock than modified nano-carbon sorbent, while the difference in their sorption capacity is not so significant. This fact, along with the convenience of working with activated charcoal, makes it the best material among inorganic ones.

3.1. Sorption of humic acids on unpretreated (native) organic materials.

The results of experiments on sorption/desorption of humic acids on lignocellulosic materials are shown in Table 2.
Table 2. Parameters of sorption of humic acids onto organic materials

| Material                          | Sorption (mg/g) | Desorption (mg/g) | Sorption capacity (mg/g) | Relative sorption capacity (mg/m²) | S_{sp} (m²/g) |
|----------------------------------|-----------------|-------------------|--------------------------|-----------------------------------|----------------|
| Cellulose                        | 1.4             | 1.2               | 0.2                      | 0.03                              | 6.5 ± 0.3      |
| Delignified wheat straw LC after water extraction | 2.4             | 1.5               | 0.9                      | 0.06                              | 16.0 ± 0.9     |
| Rice husk                        | 2.0             | 0.98              | 1.4                      | 0.16                              | 8.6 ± 0.5      |
| Lignin                           | 4.6             | 1.3               | 3.3                      | 0.33                              | 9.9 ± 0.5      |

The sorption capacity of lignocellulosic materials increases in the cellulose–lignin series. Although the specific surface area of lignocellulose after water extraction is twice as low as that of the delignified biomass, their sorption degrees are identical due to an increased lignin content in lignocellulose after water extraction. This fact is indicative of the chemical nature of sorption. The delignified biomass is simultaneously characterized by maximum desorption.

The sorption capacity of lignin-containing materials is higher than that of cellulose. Sorption capacity with respect to humic acids depends linearly on lignin content in the biomass [11], which attests to the chemical mechanism of sorption according to which the functional groups of lignin form hydrogen bonds with respective functional groups of humic acids. Hence, the ability of plant biomass to bind humic acids depends on the lignin component. For the plant biomass under study, the maximum degree of sorption is 3.3 mg HA per g of dry sorbent.

The high affinity of humic acids for lignin is attributed to the fact that humic acids and lignins contain groups of similar nature (e.g., the orthophenolic moieties). This similarity is evolutionarily reasonable, since humic acids are the products of deep conversion of lignins and flavonoids. Binding between humic acids and lignin fragments takes place via polar interactions, cationic bridges, van der Waals forces, and hydrogen bonds [13]. Alcoholic hydroxyl groups of humic acids can interact with lignin by forming p-hydroxybenzyl esteric chemical bonds [13]. Hence, it has been demonstrated that when the sorbent particles with a “lignocellulosic core–humic shell” structure are designed, humic acids bind to lignocellulosic materials by forming chemical bonds with the lignin component of the biomass. The great variety of lignocellulosic materials that are formed as industrial wastes [14] can potentially be used to produce sorbents with a “lignocellulosic core–humic cell” structure.

3.2. Sorption of Humic Acids onto the Mechnochemically Modified Lignocellulosic Materials.

One of the stages in designing particles with a “lignocellulosic core–humic shell” structure is to search for a method to enhance the sorption capacity of lignocellulosic feedstock with respect to humic acids by performing mechanochemical pretreatment. This pretreatment allows one to conduct solid-phase chemical reactions without using solvents [15]. The most promising materials were those in which lignin content on the surface was increased by mechanochemical pretreatment in a laboratory-scale mechanochemical activator (attritor) at a temperature of lignin devitrification (180°C). Under these conditions, lignin undergoes a phase transition to a rubber-like state, migrates to the particle surface, and is accumulated there.

The high lignin content on the surface, in combination with high porosity, is expected to enhance the sorption capacity of plant biomass with respect to humic acids. Wheat straw and reed biomass (lignin content being 21.7 ± 0.1 and 38.5 ± 0.3 %, respectively) were selected as study objects. Table 3 shows the sorption capacity of the native and pretreated materials with respect to humic acids.
Table 3. Sorption capacity of wheat straw and reed before and after mechanochemical pretreatment

|                                | Sorption (mg/g) | Desorption (mg/g) | Sorption capacity (mg/g) | Relative sorption capacity (mg/m²) |
|--------------------------------|-----------------|-------------------|--------------------------|----------------------------------|
| Reed biomass without activation| 7.3 ± 0.5       | 1.4 ± 0.1         | 5.9 ± 0.6                | 2.9 ± 0.3                        |
| Reed biomass (attritor, 100°C) | 7.7 ± 0.5       | 1.5 ± 0.1         | 6.2 ± 0.6                | 2.7 ± 0.2                        |
| Reed biomass (attritor, 180°C) | 0.5 ± 0.1       | 1.0 ± 0.1         | -                         | -                                |
| Wheat straw (attritor, 25°C)   | 2.0 ± 0.2       | 0.9 ± 0.1         | 1.1 ± 0.3                | 0.6 ± 0.1                        |
| Wheat straw (attritor, 180°C)  | 2.4 ± 0.2       | 0.8 ± 0.1         | 1.6 ± 0.3                | 0.5 ± 0.1                        |

The results demonstrate that the mechanochemical pretreatment of reed and wheat straw under different conditions did not significantly enhance the relative sorption capacity of these lignocellulosic materials with respect to humic acids. An increase in sorption capacity was observed for wheat straw, but this increase was found to be insignificant when the sorption capacity was recalculated per surface area. An opposite effect was observed for reed. In the experiments on sorption of humic acids from the solution, lignin was washed off the particle surface and passed into the solution, leading to an apparent increase in humic acid concentration in it. Hence, an interesting fact is that a method for bringing lignin from the surface of lignocellulosic feedstock to the solution using humic acids has been revealed. Unmodified highly lignified plant biomass is the optimal material to solve the problem of applying humic acids onto plant-derived materials.

The resulting core–shell materials exhibit high efficiency as heavy metal sorbents not only in the laboratory-scale experiments but also in full-scale ones [16]. It was demonstrated that core–shell materials can be repeatedly used up to five times; their sorption properties remain high after regeneration in the presence of 0.05 M HNO₃ [17].

4. Summary

Core–shell particles have been obtained, where humic acids act as a shell and a number of inorganic and lignocellulosic materials are used as the core. The efficiency of binding between humic acids and lignocellulosic materials directly correlates with lignin content within lignocellulosic materials. A method for passing lignin from the surface of lignocellulosic biomass to the solution using humic acids has been found. Unmodified highly lignified plant biomass is the optimal material for applying humic acids onto lignocellulosic materials. The resulting core–shell particles are promising heavy metal sorbents that can be used in natural environment objects.

5. References

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