Adsorption of Organic Pollutants from Aqueous Solutions on Cereal Ashes

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This work reports on the application of cereal ashes, from barley, oat, triticale, and wheat grains, as adsorbents for the removal of several organic pollutants: benzene, phenol, tetrachloroethylene, and toluene. The order of adsorption found for benzene and toluene on ashes was barley > oat > triticale > wheat, whereas for phenol and tetrachloroethylene, it was wheat > triticale > oat > barley. The Freundlich isotherm model has been applied to the equilibrium adsorption data.

Introduction

One of the current research activities in the world is to investigate if cereals and crop residues could be an alternative energy source to fossil fuels.[1] The identification of cereal species and varieties with high biomass yield, high combustibility, low ash content, and low potential for boiler corrosion is a priority. Annual crops such as wheat, rye, or triticale, cultivated as an alternative energy source, do not require high investment, and they are easy to rotate in the crop cycle. Cultivation, fertilization, and harvesting techniques are essential to ensure the optimal use of resources. In this way, rye and triticale are better than wheat because they have low grain losses and require less fertilizers, pesticides, and insecticides.

Emissions and efficiencies were more or less the same for energy crops as for wheat straw. A marked rise in the NO_x emission can be seen for certain plants since the protein content of the grain releases nitrogen during burning. Other factors that need to be considered are the high alkali content of the fuel, which can lead to corrosion in boilers, and the high content of heavy metals in the ashes, which means they cannot be spread on farmland. The ashes resulting from the crops combustion with coal cannot be used in the cement industry because of their high potassium content. It seems that when it comes to hard economic realities, there is a huge gap between the farmers' need for profitable production and the market prices anticipated in the energy strategies.

Producing and using biomass requires other inputs such as diesel oil, nitrogen fertilizer, and pesticides which, depending on the type, dosage, and utilization, have a negative impact on the environment compared to that of fallow fields. Economic estimations show that energy crops have high potential, so they form a major element in the long-term world energy strategy.[2] The challenge for research programs is to find the most cost-effective and least damaging way to use this resource.

If we accept that biomass can be seen in the long term as a universal sustainable replacement for fossil raw materials once the extensive research and development work has been completed and if future governments decide to use the energy of crops, ashes from combustion of biofuels should be regarded also as a resource. Therefore, the data presented in this study could be helpful with regard to the usefulness of the ashes as nonconventional adsorbents for removal of pollutants.

Table 1. Chemical Composition (wt %) of the Materials

	Al_2O_3	CaO	Fe_2O_3	MgO	MnO_2	Na_2O	P_2O_5	SiO_2	K_2O
wheat	< 0.001	0.59	< 0.001	8.10	1.80	< 0.001	82.0	7.10	0.30
barley	0.01	0.30	0.01	3.02	4.45	< 0.001	94.10	1.80	1.60
oat	< 0.001	0.14	< 0.001	3.50	0.15	< 0.001	95.0	1.50	0.25
triticale	< 0.001	0.08	< 0.001	3.70	0.82	0.006	91.10	3.61	0.07

Benzene, phenol, toluene, and tetrachloroethylene are considered as priority pollutants since they are harmful to organisms at low concentrations and have been classified as hazardous pollutants because of their potential to harm human health. Because of their toxicity, the Agency for Toxic Substances and Disease Registry, of the U.S. Department of Health and Human Services, has designated these chemicals as priority pollutants.[3]

Adsorption processes have been reported as low-cost techniques for the treatment of organic pollutants present in water waste. Activated carbons, modified clays, polymeric resins, waste materials, and zeolites have been described as adsorbents.[4]

The aim of this study is to investigate and to compare the performance and effectiveness of various cereal ashes as adsorbents for the removal of four organic contaminants present in typical water waste: benzene, phenol, tetrachloroethylene, and toluene. The Freundlich adsorption isotherm equation is applied to the experimental data to obtain information about the interaction between the organic pollutants and the cereal ashes.

Experimental

Starting Materials. The materials used in the present study are obtained from various cereal grains, wheat, barley, triticale, and oat, by the following procedure: the cereal grains are subjected to heating for 6 h at about 150 °C and then kept in a furnace for 24 h in air at 550 °C. The solids thus obtained are stored in a vacuum desiccator until required. Chemical analyses are carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Shimadzu ARL 34000 instrument. The results are presented in Table 1. Cereal ashes contain relevant amounts of plant nutrients like K, Mg, and P. In addition, ashes contain a number of elements that are beneficial to plants in small doses, i.e., micronutrients, but also generally contain small amounts of undesirable heavy metals.

SEM observations were carried out on a Philips 501 microscope. The studied samples are fixed to a holder with silver-containing lacquer. Vacuum deposition of the gold film on the ashes adsorbents is applied as the specimens have so-called material contrast.

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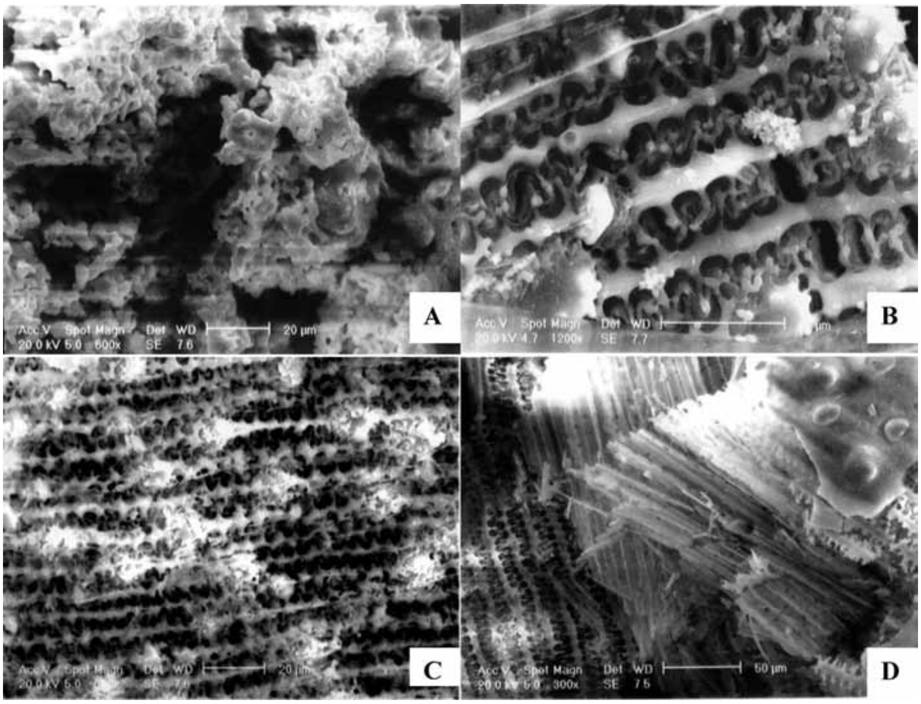

Figure 1. SEM micrographs of triticale (A), wheat (B), barley (C), and oat (D) cereal ashes.

Nitrogen (99.999 %) adsorption experiments have been performed at −196 °C using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). Before the adsorption experiments, the sample is outgassed at 120 °C for 16 h. The specific surface areas are calculated from the BET method.[5]

Adsorption Experiment Procedure. The organic compounds used in the present study as adsorbates were the following: benzene, phenol, tetrachloroethylene, and toluene. All organic compounds were purchased from the Merck Chemical Company.

The organic chemicals were freshly prepared in a solution mixture of deionized water/ethanol (80:20). To determine the equilibrium adsorption capacity of the organic compounds by the materials, 30 cm^3 of adsorbate solution of several concentrations, from (104 to 1240) $\text{mg}\cdot\text{L}^{-1}$, was placed in a flask, and 0.5 g of cereal ash was added. The flasks, at a controlled temperature of 25 °C, were sealed with a stopper and then shaken for 24 h at 200 rpm. The pHs of the solutions were those corresponding to the mixture of deionized water/ethanol used in all the cases, with no measurable variations due to the solute concentrations. After centrifugation, for 30 min at 3000 rpm, the adsorbate equilibrium concentration was measured using a JASCO UV−visible spectrophotometer at the following wavelengths: benzene, 252 nm; phenol, 270 nm; tetrachloroethylene, 201 nm; and toluene, 260 nm.

The specific adsorbed amount (q_e) of the organic chemical on cereal ashes was calculated from the initial and equilibrium concentrations according to the equation

$$q_e = V\cdot(C_0 - C_e)/m \qquad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations ($\text{mg}\cdot\text{L}^{-1}$) of adsorbates; V is the volume of the solution (L); and m is the amount of adsorbent (g). In this method, it is assumed that the change in volume of the bulk liquid phase is negligible because the solute concentration is small and the volume occupied by the adsorbent is also small. The amount of organic pollutant adsorbed on the sample was calculated based on a previously determined calibration curve.

Results and Discussion

The images obtained by SEM of the ashes are shown in Figure 1. It is clear from this figure that ashes of wheat, barley, and oat have similar structures after calcination. The structure of the ash from triticale is more irregular in shape than that in other cereals. The aleuronic cells are badly distorted, and lesions have been noted in which complete sections of aleuronic and associated endosperm cells are missing. The surface area of the cereal ashes is rather low, between (2 and 6) $\text{m}^2\cdot\text{g}^{-1}$. These values can be justified by open porous structure, as is observed in Figure 1.

The results of the adsorption experiments of organic pollutants on the cereal ashes are shown in Figure 2. By examining these figures, for all systems, the behavior is approximately linear: the sorption capacities of all the sorbents increased with increasing equilibrium concentration. The increase in the loading capacities of sorbents with increasing pollutant concentrations is due to the interaction between organic compounds and adsorbents. A comparison between the adsorption isotherms shows that there is no large difference in performance between the sorption of benzene, tetrachloroethylene, and toluene, but phenol was adsorbed less than the others. The low removal efficiencies for the adsorption of phenol observed in this study should be related to the relatively high solubility of phenol in water in comparison with the other organic compounds.

The organic pollutant adsorption isotherms can be classified within type C of the Giles adsorption isotherms classification.[6] The shape of the isotherms means that there is no strong interaction between the organic pollutants and the adsorbent. The experimental adsorption equilibrium data of organic pollutants on cereal ashes were fitted by applying the Freundlich isotherm model,[7] which is a usual model for aqueous-phase adsorption. The Freundlich model gives a representation of the adsorption equilibrium between an adsorbate in solution and the surface of the adsorbent

$$q_e = k_F\cdot C_e^{1/m_F} \qquad (2)$$

where q_e ($\text{mg}\cdot\text{g}^{-1}$) is the specific equilibrium amount of adsorbate; C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium concentration of adsorbate; and

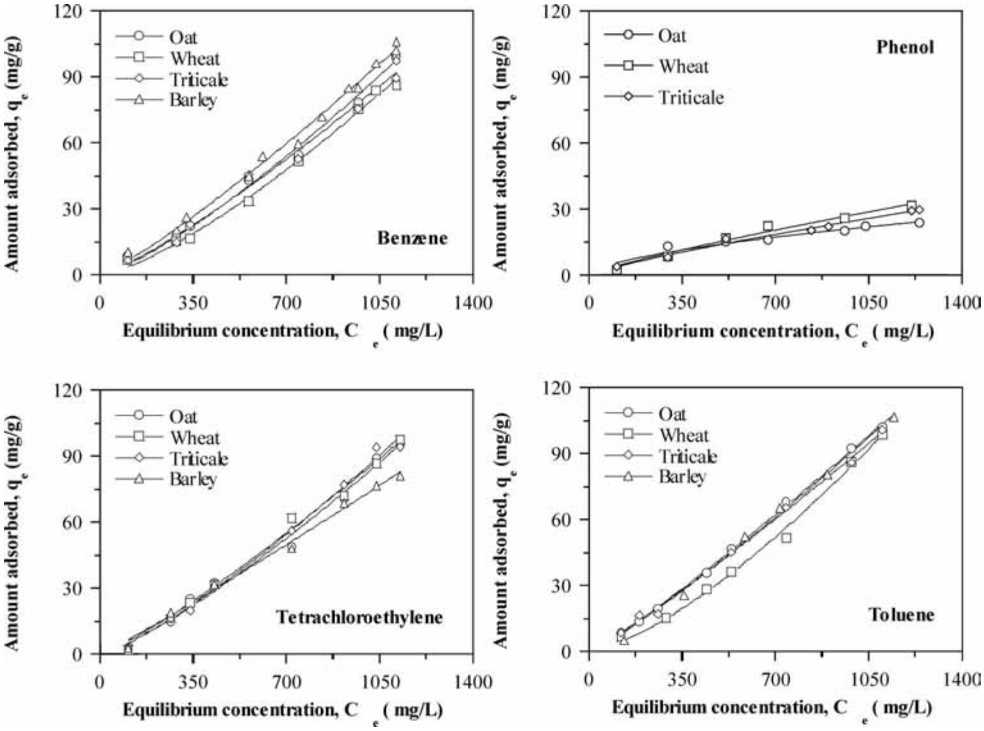

Figure 2. Equilibrium data of organic pollutant adsorption on cereal ashes.

Table 2. Freundlich Equation Parameters for Benzene, Phenol, Toluene, and Tetrachloroethylene Adsorption on Cereal Grain Ashes

	k_F (mg·g^{-1})	m_F	χ^2 (average quadratic deviation)	R (regression factor)
oat				
benzene	0.013	0.78	58	0.997
phenol	0.35	1.68	20	0.97
tetrachloroethylene	0.015	0.80	89	0.994
toluene	0.040	0.89	12	0.9993
wheat				
benzene	0.007	0.74	37	0.997
phenol	0.084	1.19	13	0.98
tetrachloroethylene	0.024	0.84	61	0.996
toluene	0.0051	0.71	34	0.997
triticale				
benzene	0.019	0.82	96	0.994
phenol	0.084	1.21	7	0.993
tetrachloroethylene	0.015	0.80	58	0.997
toluene	0.042	0.90	22	0.998
barley				
benzene	0.028	0.85	74	0.997
phenol	n.m.[a]	n.m.	n.m.	n.m.
tetrachloroethylene	0.046	0.94	44	0.996
toluene	0.032	0.87	33	0.997

[a] n.m., not measured.

k_F and m_F are empirical constants, indicative of the extent of adsorption and the adsorption effectiveness, respectively. The constant m_F gives an idea of the grade of heterogeneity in the energetic centers distribution and is related to the magnitude of the adsorption driving force.[8] High values on m_F indicate a relative uniformity in the surface. Low values of m_F in isotherms mean high adsorption at low concentrations in the dissolution. Furthermore, low values of m_F indicate the existence of a great proportion of active sites with a high energy.

The Freundlich model supposes that the adsorption surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. The Freundlich isotherm parameters are presented in Table 2. The highest k_F is obtained for the adsorption of phenol, and the lowest one is for the adsorption of benzene.

Conclusions

The preliminary studies show that waste materials from cereal ashes can be used effectively for the removal of hazardous pollutants from aqueous solution. As result of the work, the cereal ashes retain benzene, phenol, toluene, and tetrachloroethylene after a period of 24 h under neutral conditions. The interaction of the organic pollutants occurring in aqueous solutions with the surface of cereal ashes depends on the properties of the surface ashes and the solubility of the organic pollutants in water.

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