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Mechanochemically oxidized brown coal and the effect of its application in polluted water

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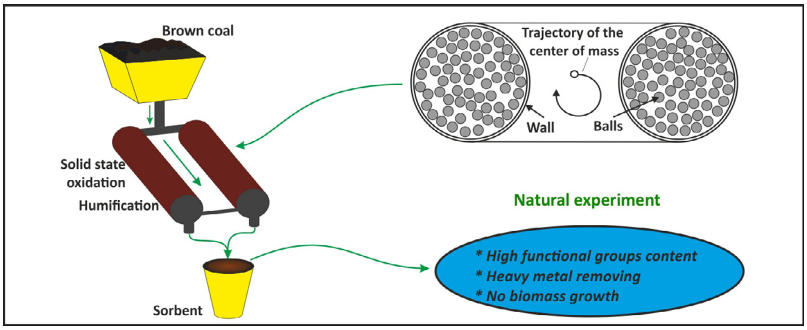
HIGHLIGHTS

- The solid phase technology of one-step synthesis of effective sorbent.
- Efficient sorbent for the removal of Cu^{2+}, Cd^{2+} and Zn^{2+}.
- Effectiveness tested in real fresh-water body.
- No eutrophication by-effect.

GRAPHICAL ABSTRACT



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ABSTRACT

The technology of mechanochemical oxidative modification of brown coal in solid phase was developed and scaled using flow-type equipment. With the oxidized brown coal (BC_{ox}), the yield of humic substances extracts increased from 23 to 70% and the content of phenolic and carboxylic groups increased by 55 and 103%, respectively. BC_{ox} performs as promising sorbent for heavy metal remediation of surface water, and its impact on the environmental fate of inorganic contaminants (heavy metals) was tested in a real fresh-water body, namely, the Novosibirsk Water Reservoir on the Ob river. Experiments were carried out with the help of meso-modeling of water pollution with a mixture of Zn(II)-Cu(II)-Cd(II). The introduction of heavy metals into water suppresses the vital activity of phytoplankton in the first few days, but the phytoplankton then adapts and begins to propagate, sorbing the pollutants. The addition of the BC_{ox} caused substantial acceleration of the withdrawal of heavy metals. The use of the BC_{ox} did not cause water blooms, distinct from sorbents based on non-oxidized humic substances with the native structure.

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Abbreviations

BC_{in}	initial brown coal;
BC_{ox}	oxidized brown coal;
BC_{alk}	brown coal after mechanical activation with sodium hydroxide;
HA_{in}	initial humic acids from initial brown coal;
HA_{ox}	oxidized humic acids from initial brown coal.

0. Introduction

Humic substances (HS) are important representative dissolved organic matter (DOM) in soil and natural water (Steinberg, 2013). Depending on the structure of HS, they are responsible for binding and transporting organic and inorganic compounds (Aiken et al., 2011; Chin et al., 1997; Choe et al., 2018; Smolyakov et al., 2015). For instance, an increase in proportion of condensed aromatic rings causes an increase in the hydrophobic properties of HS and their ability to remove organic pollutants, e.g., hydrocarbons (Haitzer et al., 1999; Perminova et al., 2001; Vaz et al., 2015). The peripheral parts of the structure of HS, namely, phenolic and carboxylic functional groups, are responsible for binding heavy metals (Tipping, 2002).

Brown coal is one of the most important industrial source of HS. The common methods of HS extraction from brown coal include the use of alkali, acids and organic solvents and are accompanied by high impact on environment (Ivanov et al., 2005). However, in the case of brown coal with high yield of HS some applications do not require extraction. One of the way to increase the yield of HS in brown coal is to use a mechanochemical treatment (Ivanov et al., 2007). Syntheses based on mechanochemical technologies are recognized as eco-friendly due to their high efficiency, and the possibility to decrease the number of stages avoiding the use of solvents (Varma, 2016; Qu et al., 2017). Mechanochemical approaches to the treatment of humin-containing natural raw materials allow chemical modification of their structure to impart the necessary properties (Turčániová and Baláž, 2000; Skybová et al., 2007; Mirzobekzoda et al., 2015). Mechanical activation is an increase in reactivity caused by mechanical action in specially designed devices such as mills and mechanical activators (Beyer and Clausen-Schaumann, 2005; Lomovsky et al., 2016). Mechanical treatment of a material with chemical reagents in the solid phase yields composites with the modified surfaces. Mechanical action on brown coal, accompanied by grinding, leads to the formation of paramagnetic centers, which are radicals formed on the surface of coal particles due to the rupture of various chemical bonds (Proidakov, 2009). However, mechanochemical action involves not only an increase in active surface of the components in mixture and a decrease in diffusion hindrance but also chemical transformation of the target substances (Boldyrev, 2006; Wei et al., 2009). Due to the persistence of humic material in soil and in geological deposits over many years, the majority of the active groups of humic acids are already involved in various chemical interactions (Aiken et al., 1985). Mechanochemical action allows one not only to purify the available active groups in humic acids (this most frequently involves the deprotonation of protonated acid groups via the formation of salts) but also to increase their number through formation of new groups. The current technological interest in mechanochemical methods arises because mechanochemical reactions in the solid phase allow modification of the macromolecules of humic acids at specific bonds to yield products enriched with humic fragments with the prevailing content of the required functional groups (Savel'eva et al., 2013; Lomovsky et al., 2004).

Successful accomplishment of the listed processes in specially designed flow devices will allow production at the industrial and semi-industrial scale of humin-containing sorbents characterized by a high content of phenolic and carboxylic groups. Humic acids are prone to oxidation and are good traps for oxidative radicals, for example HO· (Westerhoff et al., 1999; Zherebtsov et al., 2015). A solid-phase oxidizer is necessary for mechanochemical reactions. Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) can be used as the oxidizer in this situation (McKillop and Sanderson, 1995). It was established previously (Urazova et al., 2014) that mechanochemical treatment of brown coal in the presence of sodium percarbonate causes an increase in the extractability of humic substances with both water and alkali solutions. This process is accompanied by further oxidation of brown coal and an increase in the content of phenolic and carboxylic groups, while the molecular mass distribution of humic acids remains unchanged. The products of this mechanochemical reaction exhibit high sorption towards heavy metals.

The goals of this work are to develop and scale up the technology of solid-phase mechanochemical oxidation of brown coal and to examine the effect of its product on the redistribution and environmental fate of inorganic pollutants (heavy metals) in a real fresh-water reservoir.

1. Materials and methods

1.1. Brown coal treatment

Brown coal from the Itatskoye deposit of the Kansk–Achinsk coal basin (below referred to as BC_{in}) was used as the raw material. It contains approximately 1% water-soluble humic acids, 25% alkali-soluble humic acids extractable via complete alkaline extraction and 10,7% of ash. The technology of mechanochemical oxidation of brown coal was developed using