

Removal of Mn²⁺ from water by bentonite coated with immobilized thin layers of natural organic matter

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ABSTRACT

A bentonite-based composite was synthesized by applying thin coatings of natural organic matter onto bentonite particles in aqueous suspension. Natural organic matter, mostly comprised of humic acids, was isolated from peat by alkaline extraction. It was insolubilized and immobilized on bentonite by heating at 350 °C in an inert nitrogen atmosphere. The composite obtained was then used to remove manganese from aqueous solutions. The results showed that manganese was removed significantly; the degree of removal was above 94% for initial concentrations of manganese from 0.250 to 10 mg/l. The effect of initial pH on manganese removal, dissolution of immobilized organic matter as well as the changes of pH and conductivity of water after treatment with composite were examined and explained.

Key words | bentonite, composite material, manganese removal, natural organic matter

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INTRODUCTION

The problem of the presence of heavy metals in drinking water is becoming more and more significant; thus many materials have been examined for the effective removal of harmful substances from water. They include activated carbons, activated alumina, ion-exchange resins, coals, zeolites, clay minerals and other aluminosilicates, and peat (Doula 2006).

Manganese is a heavy metal which constitutes about 0.1% of the Earth's crust in the form of silicates, carbonates, sulphates, oxides and borates; it cannot be found in its elementary form in nature (Newcombe & Dixon 2006; Buamah *et al.* 2008). The abundance of manganese in the environment is influenced by anthropogenic factors as well, for example, mining activities and the decomposition of products that contain manganese, such as steel alloys, fertilizers, fungicides, batteries, food additives and unleaded gasoline (Newcombe & Dixon 2006). The amount of manganese in water depends on the geochemical composition of the terrain that water runs through or that is in pool form, and to a lesser extent on fauna composition and possible anthropogenic

factors. A median manganese level in surface waters is 16 µg/l, with 99th-percentile concentrations of 400–800 µg/l (WHO 2008). Due to the reducing conditions in groundwater and some lakes and reservoirs, high manganese concentrations have been reported. They are up to 1.3 mg/l in neutral groundwater and 9.6 mg/l in acidic groundwater (ATSDR 2000). The important oxidation states of manganese in nature are II, III and IV which together with pH value and anions present determine its mobility in the environment and its solubility in water (Buamah *et al.* 2008). Manganese is an essential element for humans and animals, as it is a constituent of enzymes (Sharma *et al.* 2007). It has an important role in calcium and phosphorus metabolism, as well as in the maintenance of reproductive function in organisms. According to World Health Organization recommendations, concentrations below 0.05 mg/l are usually acceptable to consumers, although this may vary with local circumstances. Even though it belongs to the group of elements with least toxicity, significantly higher concentrations than recommended in long-term exposure can lead to respiratory and central

nervous system damage (the symptoms are similar to Parkinson's disease). Higher concentrations can cause DNA damage, chromosomal aberration in cells of mammals and skin changes (WHO 2004). Moreover, aesthetic problems occur since manganese can give water an unpleasant taste, odour and colour, and cause brownish-black staining of laundry, starting from the concentration of 0.15 mg/l.

For manganese removal in the preparation of drinking water, several technologies have been developed: ion-exchange, reverse osmosis, ultrafiltration, electro dialysis, adsorption on specific adsorbents and oxidation (Doula 2006; Newcombe & Dixon 2006). Oxidation and precipitation are the most common methods to remove Mn(II). Such methods are based on oxidation of Mn(II) to insoluble manganese dioxide, followed by clarification and/or filtration (Voorinen 1988; US EPA 2003; Roccaro *et al.* 2007). Oxidation in rapid sand filtration is a commonly applied technology for manganese removal, and most drinking water production plants use rapid sand filters for the removal of manganese from ground water. However, the rate of manganese oxidation is very low at pH values below 9 (Buamah *et al.* 2009). The product water is satisfactory when a strong oxidant are used, but the cost of the oxidant is very high (Ellis *et al.* 2000). Enhanced filtration can be carried out by conditioning the filter media with permanganate to form a manganese oxide coating on the surface of the media or by using greensand (García-Mendieta *et al.* 2009). Specifically, microfiltration after oxidation with potassium permanganate (KMnO₄) and manganese sand filtration, as well as ultrafiltration with in-line prechlorination, have been successfully applied to remove manganese from groundwater (Ellis *et al.* 2000; Rahman *et al.* 2000; Teng *et al.* 2001; Choo *et al.* 2005). A number of adsorbent materials have been studied for their adsorption capacity for manganese removal, for example: montmorillonite–3.22 mg/g (Abollino *et al.* 2003); granular activated carbon–2.54 mg/g (Jusoh *et al.* 2005), clinoptilolite–7.69 mg/g (Doula 2006); natural zeolitic tuff from Vranjska Banja in Serbia–8.61 mg/g (Rajic *et al.* 2009).

This paper describes the synthesis of a new bentonite-based composite material by applying thin coatings of natural organic matter, obtained by alkaline extraction from peat, mostly comprised of humic acids. Humic acids have high complexing ability for various heavy metal ions, but it

is difficult to use them as the sorbent because of their high solubility in water. However, they form stable complexes with the inorganic constituents of bentonite (montmorillonite, quartz, oxides, etc.) and can be additionally insolubilized and immobilized by heating at 350 °C. After immobilization, humic acids represent an important sorbent for heavy metals, pesticides and other harmful ingredients from water. Humic acid are insolubilized by condensation of carboxylic and phenolic hydroxyl groups. Therefore, the aim of the paper was to remove manganese from aqueous solutions by treating it with a synthesized composite as well as to study and explain the mechanism of composite interaction with manganese aqueous solutions. The composite does not release a significant quantity of organic matter in to the water because it is tightly bonded to the bentonite surface (Ayari *et al.* 2005; Kolokassidou *et al.* 2007; Ghosh *et al.* 2009). The degree of manganese removal was more than 94% at a range of initial manganese concentrations from 0.250 to 10 mg/l.

MATERIAL AND METHODS

Chemical composition of bentonite

In order to perform reliable composite synthesis, the chemical composition of the matrix must be well known. For this reason 1 g of matrix sample (Ca²⁺-bentonite) was dissolved in an acid mixture HF/HCl, and then, the solution was steamed until dry several times with HCl to remove HF. The dried residue was dissolved in 100 ml of deionised water and analysed by inductively coupled plasma optical emission spectrometry, using an ICP-OES Spectrometar iCAP 6000 (Thermo Electron Corporation). Concentration of Si was determined after melting 0.5 g of bentonite with 5 g of anhydrous Na₂CO₃, as described elsewhere (Jeffery *et al.* 1989). Cation exchange capacity and specific surface area were estimated by the methylene blue method (Pansu & Gautheyrou 2006; Yukselen & Kaya 2008).

Alkaline extraction of peat

The peat used was formed thousands of years ago by the breakdown and deposition of plant residues (mosses, ferns

and partly cane, in the conditions of a mountain climate, at an altitude of 1,150 m of the Pester plateau (Serbia). Slightly mineralized Pester peat contains: organic matter–89%; total nitrogen–2.41%; total potassium–0.18%; total phosphorus–0.18%; and other macro, meso and micro elements–8.23%.

The alkaline extraction was performed by the following procedure. Twenty-five grams of peat, dried at room temperature, was transferred to a 600 ml glass beaker and 1 M HCl was added up to pH = 1–2. The suspension was stirred by a magnetic stirrer for 1 h. The supernatant was decanted, and 1 M NaOH was added to the residue up to pH = 11. The system was left at room temperature for 24 h, and then the supernatant was separated by decanting and acidified with 6 M HCl up to pH = 1. The suspension was left overnight, and then the precipitate was separated by centrifuging and washed with distilled water. The organic matter obtained was dried at room temperature.

Synthesis and characterization of composite

In a 600 ml glass beaker, 1.5 g of organic matter was dissolved in 250 ml 0.1 mol/l KOH and stirred for about 30 min, and 20 g of bentonite was added. The suspension was stirred for 16 h. Thereafter, under vigorous stirring of the suspension, 6 M HCl solution was added in drops up to pH = 2. The glass was covered by aluminium foil and left at 70 °C for the next 2 h. After cooling to room temperature and filtering, the solid phase was dried and thermally treated in an inert nitrogen atmosphere at 350 °C for 1 h. The composite obtained was crushed in an agate mortar, washed with 0.1 M HCl and hot distilled water (until free of Cl[−]) and dried at 105 °C. The composite was passed through a 120 mesh sieve (particles size less than 125 μm) and the resulting dark brown-black powder was used for adsorption experiments and further examination.

Fourier transform infrared (FTIR) spectra and surface images were obtained by ATR-FTIR spectrometer Bruker Tensor-27 equipped with a FTIR Bruker Hyperion-1000/2000 microscope. The total content of acidic groups on the surface was determined by conductometric titration of a suspension containing 1 g composite in 250 ml of distilled water, containing 1 mM NaCl as background electrolyte

with 0.053 M NaOH solution. The value of the total acidic group content was calculated using the following equation:

$$X = \frac{C_t \cdot V}{m} \quad (1)$$

in which, X is the total acidic group content in μmol/g; C_t is the concentration of NaOH (μmol/l); V is the volume of NaOH added to reach the equivalent point (l); m is the mass of the sample dried at 105 °C (g). All conductometric measurements were performed with a HACH sensION5 conductometer.

The release of organic matter from the composite in water depending on the solution pH was estimated by determining the permanganate number. A suspension was prepared by mixing 0.2 g of composite and 100 ml of distilled water containing 1 mM Na₂SO₄ as the background electrolyte. The pH was adjusted to the desired values by adding 0.1 and 0.01 M H₂SO₄ and NaOH. After 60 min contact, the suspension was filtered through blue band filter paper and the turbidity of filtrate was determined with a WTW turbidimeter 3551R. The permanganate number determination was carried out by the procedure described elsewhere (Nissinen *et al.* 2001).

Experimental procedure for Mn²⁺ removal from model water

Aqueous solutions of manganese were prepared by dissolving MnCl₂·4H₂O in distilled water. The following manganese concentrations were obtained: 0.250; 0.490; 1.0; 2.5; 5.0; 10.0 mg/l, and the initial pH and conductivity were measured. In 50 ml of each solution 0.1 g of composite was added and the suspension was occasionally stirred during 20 min at the temperature of 20 °C. Subsequently, suspensions were filtered, and then, pH and conductivity were measured. The concentration of manganese was determined by the ICP-OES method at λ = 259.373 nm, and the adsorption of manganese under equilibrium conditions (equilibration period of 2 h at pH 6.5) was studied. The effect of different initial pH values on manganese removal was examined as well. All chemicals used in the experiments were of analytical purity.

RESULTS AND DISCUSSION

After the dissolution of 1 g of bentonite in 100 ml of deionised water, the following elements were qualitatively detected: Al, Fe, Mg, B, Ba, Bi, C, Ca, Cr, Cu, S, Si, Ti and Zn. The following elements were quantitatively detected and they are given as oxides in wt%: 51.2 SiO₂, 26.86 Al₂O₃, 1.27 MgO, 2.30 Fe₂O₃, 1.44 CaO, 2.07 K₂O, 0.75 Na₂O, 0.1 MnO. The cation exchange capacity and specific surface area of bentonite are 54.75 meq/100 g and 470 m²/g, respectively.

The ATR-FTIR spectrum of the composite (600–4,000 cm⁻¹) and the photograph of the surface from which the spectrum was recorded are shown in Figure 1.

In the ATR-FTIR spectrum of composite absorption at 3,620 cm⁻¹ due to stretching vibration of structural OH groups of bentonite is observed. The broad peak at 3,430 cm⁻¹ corresponds to the H₂O stretching vibration with a shoulder at 3,250 cm⁻¹, due to an overtone of the vibration of water observed at 1,635 cm⁻¹. The peak around 1,310 cm⁻¹ is due to the Si–O stretching vibrations and the peak at 634 cm⁻¹ is assigned to coupled Al–O and Si–O out-of-plane vibrations. A sharp peak at 798 cm⁻¹ and the observed absorption peak in the range 1,871–1,876 cm⁻¹ confirm quartz in the sample. The C–H stretching vibrations of the methylene groups absorb at 2,850–2,920 cm⁻¹; C=C

aromatic ring vibrations are seen at 1,534 cm⁻¹, but the peak from C=O stretching vibrations is overlapped by other peaks and cannot be distinguished in the region from 1,650 to 1,750 cm⁻¹.

A small peak at 1,510 cm⁻¹ represents the N–H bending vibration from amide II. The proteinaceous fraction of natural organic matter could be detected from the peaks observed near 1,680 and 1,570 cm⁻¹ (amide I and II).

The result of conductometric titration is given in Figure 2. The equivalence point was obtained by the extrapolation of the first and second linear part of the titration curve. The value of the total acidic group content, calculated according to Equation (1), is 215.18 μmol/g.

The treatment of manganese aqueous solutions with composite for 20 min produced the results shown in Table 1.

The experimental data of manganese adsorption onto composite are very well fitted by the Freundlich isotherm model (Figure 3) with a very high correlation coefficient value of 0.9948. The good agreement of experimental data with the Freundlich model indicates that there are several types of adsorption sites on the surface of the composite. The amount of adsorbed Mn(II) increases rapidly in the first region of adsorption isotherm and then the slope of isotherm gradually decreases in the second region. The adsorption capacity of composite is 11.86 mg/g, at an equilibrium manganese concentration of 16.28 mg/l.

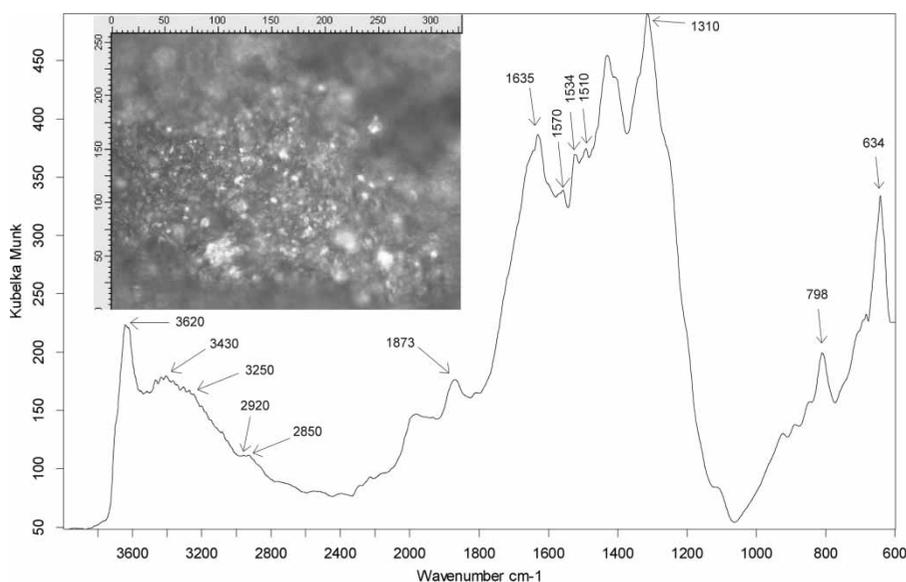


Figure 1 | ATR-FTIR spectrum and the corresponding photograph of composite surface recorded by ATR-FTIR microscope (250 μm × 350 μm).

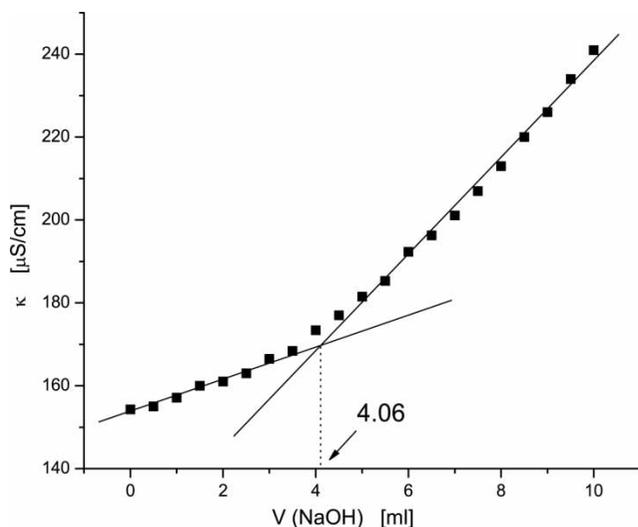
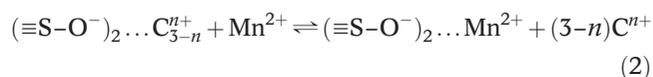


Figure 2 | The conductometric titration of composite suspension (1 g in 250 ml of 1 mM NaCl solution as background electrolyte) with 0.053 M NaOH.

During the thermal treatment in nitrogen at 350 °C, the condensation of carboxyl and adjacent alcohol and phenol groups occurs. In this way the solubility of organic matter immobilized on bentonite matrix surface decreases (Ghosh et al. 2009). Moreover, some carboxyl groups are decomposed by decarboxylation, releasing CO₂ and CO. However, despite this, some oxygen functional groups remain on the surface, and these groups act as sites that bind bivalent manganese forming inner-sphere complexes.

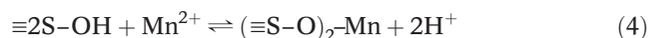
Besides organic functional groups, there are also SiOH and AlOH groups on the sites of crystal grain breaks, as well as permanent negative charge due to isomorphic substitution in clay minerals. They all contribute to the reduction of manganese concentration in the aqueous solution. Manganese retention by the formation of outer-sphere

complexes, including ion exchange, can be shown by Equation (2) (Doula 2006):



in which C represents the cation that is exchanged.

The formation of inner-sphere complexes is represented by the Equations (3) and (4) and involves the release of hydrogen ions and the change of solution pH.



According to these equations, it can be concluded that the pH value of the solutions decreases after the treatment. However, the opposite phenomenon can be observed experimentally (Table 1). The explanation for this is that hydrogen ions which are released during manganese retention participate in the protonation of surface groups, thus:



Therefore, the pH value of the Mn²⁺ aqueous solutions after treatment with composite had a higher value than the initial pH. This indicates that more hydrogen ions are bound to the surface than released by manganese binding – that is, the composite exhibits an amphoteric character due to the

Table 1 | The results of water analysis before and after treatment with composite

Before water treatment			After water treatment			
C ₀ (Mn) mg/l	pH	Conductivity μS/cm	pH	Conductivity μS/cm	C (Mn) mg/l	%Mn adsorption
0	6.43	8.01	6.67	11.43	0	0
0.250	6.37	9.57	7.11	13.76	0.0030	98.8
0.490	6.32	10.67	7.15	15.31	0.0039	99.2
1.0	6.30	14.67	7.12	31.10	0.0090	99.1
2.5	6.20	20.70	6.96	37.20	0.0187	99.25
5.0	6.19	32.80	6.83	49.40	0.0646	98.71
10.0	6.16	55.30	6.70	68.90	0.5314	94.69

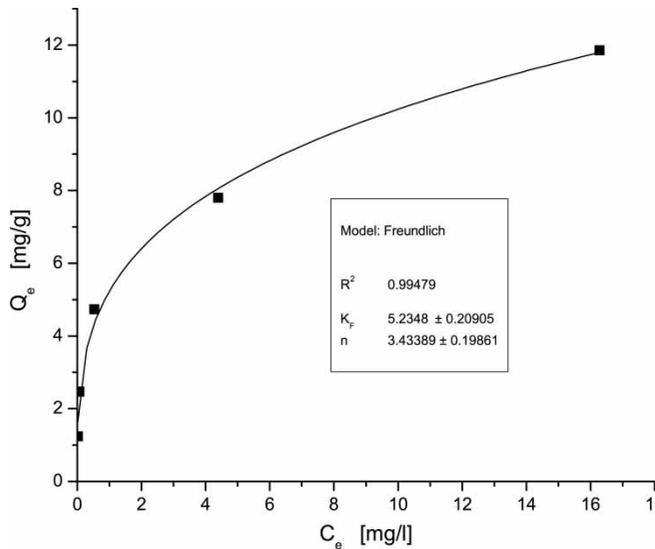


Figure 3 | Freundlich adsorption isotherm for manganese adsorption onto composite.

surface sites that act either as proton acceptors or as proton donors.

Organic matter decreases the point of zero charge value of bentonite and neutralises positive electric charge that comes from interlaminated cations, thus increasing composite affinity to manganese, even at lower pH values (Zhuang & Yu 2002). Figure 4 presents the pH dependence of residual Mn concentration, for the initial Mn concentration of 5 mg/l. The residual concentration of Mn

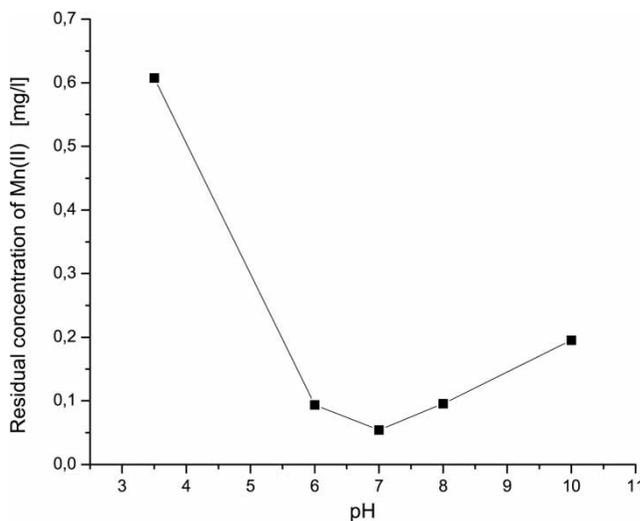


Figure 4 | Residual concentration of Mn(II) as a function of model water pH.

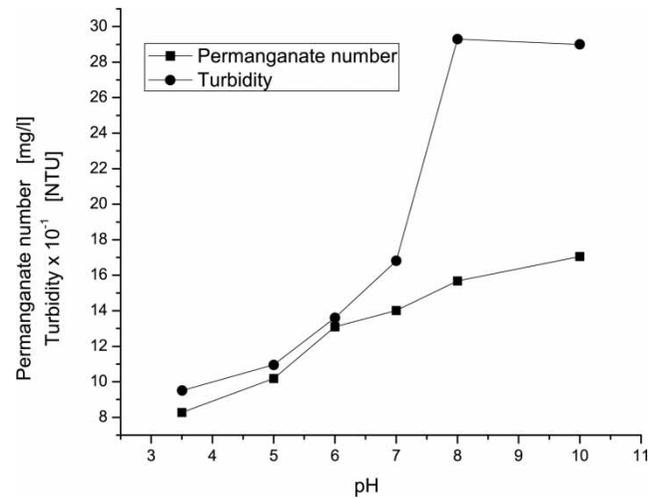


Figure 5 | Permanganate number and turbidity of filtrate as function of pH (0.2 g of composite and 100 ml of 1 mM Na₂SO₄ as background electrolyte).

decreases gradually with pH increasing in the range of 3.5–7 and then increases in the range of 7–10, with the apparent minimum at pH 7.

The increase of pH value has a dual effect on the removal of manganese. The increase of the pH value favours manganese removal due to increase of the number of deprotonated sites that are available for the binding of manganese. However, there is an increase in the solubility of organic matter which has been applied on the bentonite particles. The dissolved organic matter (humic acids) reacts with manganese, forming complexes which bear a negative charge and have a weaker binding affinity for the composite surface than Mn²⁺. Figure 4 indicates two opposite effects of the pH on manganese removal. The pH dependence of released organic matter (expressed as permanganate number) and turbidity (nephelometric turbidity units, NTU) of solutions are shown in Figure 5.

The released organic matter contributes to the increased turbidity at higher pH values.

CONCLUSIONS

By chemical and thermal procedures, the immobilization of organic matter occurs on bentonite matrix surfaces in the form of non-uniform thickness layers. The resulting composite possesses strong affinity for manganese, even at low pH

values. Organic oxygen and nitrogen groups, as well as aluminol and silanol groups on the sites of bentonite crystal grain breaks are the main surface sites where manganese binding occurs forming inner- and outer-sphere complexes. The experimental data of equilibrium adsorption of manganese on the composite are very well fitted by the Freundlich isotherm model. After manganese retention, the pH value of the solution increases since negatively charged sites bind hydrogen ions, thus decreasing their concentration in the solution. Therefore, the composite exhibits amphoteric character. Composite can be easily obtained in the form of granules or flakes that can be used as filter media in columns for purification of water containing manganese and other heavy metals in acidic and neutral pH. The increase of pH increases the solubility of organic matter and turbidity of the water. Therefore, purified water cannot be used as drinking water without additional treatments.

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