Hybrid Adsorbent for Removal of Cd(II), Cu(II), Pb(II) and Zn(II) from Waters Using Submersible Device

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Authors' contributions

This work was carried out in collaboration between both authors. Author BSS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author AKS managed the analyses of the study. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Mesoporous carbon and humic acid - native and oxidized with 5% or 15% hydrogen peroxide - were used to obtain hybrid adsorbents MC-HA, MC-HA5, and MC-HA15, respectively, for removing certain metal ions from water. Fine particles of the hybrid adsorbents were characterized by various methods. The concentration of the functional groups capable of binding metal cations in the hybrid adsorbent increased from 1.2 mmol/g in MC-HA to 1.8 mmol/g in MC-HA5 and MC-HA15. The adsorption capacity depends on pH, and at pH 6.0, it has the following order (mmol/g): Cu(II) (1.0) > Pb(II) (0.65) > Zn(II) (0.46) > Cd(II) (0.38). The adsorption process is fast and reaches the equilibrium at low concentration. The Langmuir isotherm fits the experimental adsorption data better than the Freundlich model. Prepared adsorbents were fixed on a highly porous matrix to obtain a material suitable for simple submersible devices. A high efficiency of multi-metal removal (96.1-100%) and recovery (83.5-100%) by MC-HA5 remained in at least five consecutive adsorption-desorption cycles of model wastewater treatment. The possibility of its use for the remediation of contaminated reservoirs is also shown in a full-scale experiment.

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1. INTRODUCTION

Water pollution by toxic metals has become one of the most severe environmental problems today [1]. Among the numerous methods proposed for removal of toxic metals from wastewater, adsorption is one of the most effective, economical, and eco-friendly methods [2-10]. The important advantages of this method are also the ability to regenerate adsorbents and the possibility of metal recovery following adsorption. Various materials including activated carbon, minerals, metal oxides, biomass, agricultural waste, and polymeric materials have been employed as adsorbents of toxic metals. In general, the higher the concentration of surface functional groups (SFGs) and the specific surface area of the material, the higher its sorption capacity. So man-sized materials with a high surface area and special properties have been developed as high-efficiency adsorbents, but the difficulty of solid–liquid separation limits their practical application.

To improve their applicability in real wastewater treatment, recent research has focused on the development of composite or hybrid adsorbents that combine the desirable properties of each of their components [5,11-17]. One approach is to use porous agro-based plant waste [11] or artificial polymeric materials [12] of a large particle size to produce adsorbents that are suitable for column-based filtration techniques. Another approach is based on the use of magnetic nanoparticles that can be separated from the solution using an external magnetic field instead of the filtration procedure [13-18]. Although there has been clear progress in this area over the past decade, many difficulties still remain with regard to the use of hybrid adsorbents for the treatment of large volumes of low-concentration wastewater and natural water contaminated with toxic metals.

Cadmium and lead are highly toxic metals, and copper and zinc refer to potentially hazardous metals whose concentration in wastewater and natural water is strictly regulated [19,20]. Therefore, effective adsorbents to remove these metals from contaminated water are needed. Typically, these metals are present together in industrial wastewater, as well in the waste products of the ore mining industry. Since the resulting multi-metal aqueous solutions are large in volume, only simple flow or submersible devices can be used to process them. These circumstances should be taken into account when choosing suitable adsorbents.

Previously, it was shown that hybrid biosorbents based on mesoporous carbon (MC) and humic acids (HAs) can be applied in immersion devices for the remediation of water bodies polluted by potentially harmful metals, which can result from various nonpoint sources or accidental spillages occurring in industrial and mining areas [21,22]. Hybrid adsorbent can also be affixed to the surfaces of natural mosses in the form of large aggregates. MC was chosen as an adsorbent because of its high surface area, porous structure, excellent chemical and mechanical stability, and special surface reactivity. HAs of natural origin, having different SFGs capable of effectively binding metal cations, are cheap and environmentally friendly raw materials [23,24]. However, the mechanical and chemical properties of HAs limit their use as an individual adsorbent because they have a low density and rigidity and become partially soluble at a pH greater than 6. The combination of HAs with MC allows these shortcomings to be overcome. The same result was obtained by combining HAs with Fe_3O_4 nanoparticles [14].

In this study, new hybrid adsorbents based on MC and HAs were examined for use in the removal and recovery of Cd(II), Cu(II), Pb(II), and Zn(II) from aqueous solutions. First, to increase the concentration of SFGs, the HA was treated with H_2O_2. The physical and chemical characteristics of the adsorbents obtained as fine particles were studied. Batch kinetic and isothermal experiments were performed for single-metal solutions. Secondly, to obtain adsorbents suitable for flow and submersible devices, fine particles of the adsorbents were fixed onto a highly porous polymeric matrix. These matrices were used to evaluate the efficiency of the removal and recovery of metals from multi-metal solutions simulating wastewater (in a laboratory experiment), and from contaminated water bodies (in a field experiment).

2. MATERIALS AND METHODS

2.1 Preparation of Hybrid Adsorbents

The starting materials for the preparation of the hybrid adsorbents were the MC material

Technosorb (Institute of Hydrocarbons Processing of the SB RAS, Russia) and HAs of natural origin produced from brown coal (Itatskoe Field, Russia) by a mechanochemical treatment [25]. In this study, the HAs were additionally oxidized with 5% or 15% hydrogen peroxide in order to vary the content of SFGs. This procedure was performed as follows. A 100-g sample of HA was added to 1 L of mixed solution containing 5% or 15% H_2O_2 and 1 M HCl. The mixture was stirred at 40-60°C for 2 hours, then the solution was filtered, and the oxidized HA was washed with distilled water and oven dried at 80°C. The MC and initial or oxidized HA were used for a one-step preparation of the hybrid adsorbents by mechanochemical treatment. For this preparation, the MC was mixed with initial or oxidized HA in a 1:1 mass ratio and mechanically treated for 10 min. in a high-energy planetary ball mill (AGO-2, Russia). The acceleration of the milling bodies was 300 m/s^2. The milling bodies consisted of 200 g of 5-mm stainless steel balls. After this treatment, the size of the adsorbent particles was less than 0.1 mm. The resulting hybrid sorbents - containing the initial HA and the HA oxidized with 5% or 15% H_2O_2 - were designated as MC-HA, MC-HA5, and MC-HA15, respectively. Fine particles of each sorbent type were physicochemically characterized.

As further studies showed, the sorption capacities of MC-HA5 and MC-HA15 were similar. Therefore, a cheaper MC-HA5 adsorbent was used to produce a material suitable for use in submersible devices. Fine particles of MC-HA5 were fixed onto a highly porous polymeric matrix (Syntepon, Russia) as follows. The matrix (with a size of 60×60×0.4 cm, a volume of ~1400 cm^3, and an initial mass of 108 g) was treated with a suspension of MC-HA5 (60 g) in an acidified aqueous solution (1.5 L, pH 3), with the addition of 0.5 g of the polytetrafluoroethylene F-4D (URALCHEM, Russia) as a binder. The matrix was placed in a container, filled with a solution, and left for 0.5 hours. Then, the matrix was removed, and the excess liquid was allowed to drain. The flowing liquid was transparent - that is, the hybrid adsorbent was completely fixed on the highly porous polymeric material. This was confirmed by the fact that after drying at 80°C, the mass of the material obtained (168.5 g) corresponded to the sum of the masses of the initial matrix (108 g) and the adsorbent (60 g). Thus, the proportion of adsorbent fixed to the porous matrix was about 35% wt. Fig. 1 shows the general and SEM images of the initial matrix and matrix with fixed MC-HA5. As Fig.1 *d*

suggests, the fine particles of MC-HA5 up to 100 µm in size form aggregates on the surface of the polymeric fibers. It should be noted that the strong fixation of the adsorbent onto the polymer matrix was maintained during multiple adsorption-desorption cycles.

2.2 Characterization of the Samples

The physical and chemical characteristics of fine particles of MC-HA, MC-HA5, and MC-HA15 were studied by standard methods. The specific surface areas and total pore volumes were determined by N_2 adsorption (Sorbtometer-M, Russia) using the Brunauer, Emmett and Teller (BET) method. The surface morphologies were characterized by scanning electron microscopy (SEM) using a Hitachi S3400N Scanning Electron Microscope (Hitachi, Japan). Fourier transform infrared (FTIR) spectra of the adsorbents were recorded on a SCIMAR FTS 2000 Fourier-IR spectrometer (USA) in the range 4000–400 cm^{-1}. An elemental analysis of the sorbents was carried out using a Euro EA 3000 analyzer (C, H, N, S) and a GRAND spectrometer (Russia, Si, Ca, Mg, Fe and other microelements). The concentrations of Cd(II), Cu(II), Pb(II), and Zn(II) in the solution were determined by the method of stripping voltammetry (TA-Universal, Russia) with an uncertainty of ±5%. All of the chemicals were of analytical grade.

2.3 Evaluation of the Acid–base Characteristics

To evaluate the effects of the oxidation of the initial HA with H_2O_2 on the content of acid-base SFGs, the potentiometric titration of protonated samples of MC-HA, MC-HA5, and MC-HA15 with 1.0 M KOH was carried out, using 1.0 g in 50 ml of 0.01 M KNO_3 as background electrolyte. This procedure was performed in duplicate under a nitrogen atmosphere in a pH range of 2.7 to 9.8 at room temperature (20±1°C), using a pH meter (Multitest, Russia) with an uncertainty of ±0.003 pH. The program ProtoFit 2.1 [26] was used for the calculation of the constants (pK_a) and concentrations C (mmol/g) of the acid-base SFGs from the potentiometric data.

2.4 Adsorption Experiments

All the kinetics and equilibrium batch experiments were carried out in duplicate at room temperature (20±1°C) with stirring (200 rpm), using the same dose of adsorbent (50 mg
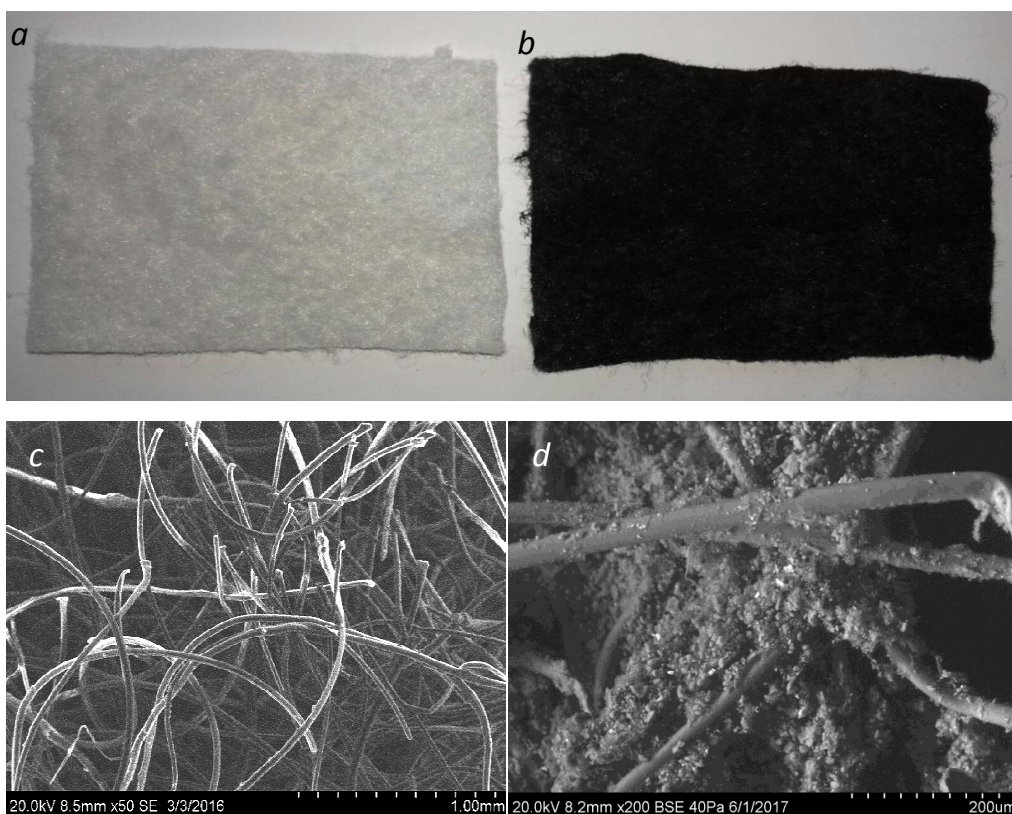
Fig. 1. General and SEM images of the initial polymeric matrix (*a*, *c*) and matrix with fixed MC-HA5 after five cycles of metals sorption-desorption (*b*, *d*)

in 100 ml of solution) and 0.01 M KNO_3 as background electrolyte. Prior to the introduction of the metals, the adsorbent suspension was stirred for 2 hours to swell the dry adsorbents. The working solutions of $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ were obtained by diluting stock solutions of each metal salt. To avoid the formation of metal hydroxides precipitates in the solutions at different pH values, the upper level of the metal concentrations had been previously estimated on the basis of chemical-thermodynamic modeling using MINTEQ software [22]. Taking these factors into account, the adsorption capacities of Cu(II) and Pb(II) were studied at pH 5.0 and 6.0, Zn(II) at pH 5.0, 6.0 and 7.0, and Cd(II) at pH 5.0, 6.0, 7.0, and 8.0.

The kinetics and isothermal studies for all the metals were performed at a constant pH = 6.00±0.02 which was maintained by microadditivies of HNO_3 or KOH. The effect of the contact time on the adsorption processes was studied in 5-180-min. intervals. After a specific contact time, the samples (~1 ml) were

drawn through a 0.45- μm-pore membrane filter. The filtrate was analyzed for its metal concentration in triplicate, using stripping voltammetry. The concentration q_t (mg/g) of metal adsorbed at time *t* was calculated by

$$q_t = (C_i - C_t)\,(V/M)\,, \tag{1}$$

where C_i and C_t are the initial and measured (at time *t*) concentrations in solution, respectively; *V* is the volume of the solution in *L*; and *M* is the mass of the adsorbent in g.

It was found that the absorption of all the metals on the hybrid adsorbents occurred quickly and was almost complete in 30-40 min. Hence, a contact time of 3 hours was used for the adsorption equilibrium experiments.

2.5 Regeneration and Reusing

The possibility of reusing hybrid adsorbents in submersible devices when processing the model wastewater was studied in successive adsorption-desorption cycles. A dry, porous

polymer matrix (7×8 cm) with 1 g of MC-HA5 was fixed vertically in a container with 100 ml of distilled water, where it was kept stirred for 2 hours at pH 3.5 to allow for swelling. Then, the stock metal solutions were introduced, and the volume of the solution was adjusted to 150 ml. The initial concentrations of the resulting multi-metal solutions were 30, 30, 30, and 15 mg/L for Cu(II), Pb(II), Zn(II), and Cd(II), respectively. The contents were stirred at 100 rpm for 3 hours, with a gradual adjustment of the pH to 6.0 with 0.1 M KOH. Then, the matrix was removed and washed with distilled water for the subsequent desorption of metals with 0.05 M HNO_3 at the final pH of 1.5. This procedure was performed for five consecutive cycles of adsorption-desorption.

2.6 Field Experiment

The purpose of the field experiments was to evaluate the possibility of reusing the hybrid adsorbents for the remediation of water bodies contaminated with toxic metals. Two full-scale experiments were carried out in the summer of 2016 in the Novosibirskoye Reservoir, using minicosms placed within the reservoir as described [22]. This reservoir was chosen for the field experiments because its water chemistry (Table 1, [27]) is similar to that of many other fresh reservoirs. The main cations are Ca^{2+} and Mg^{2+}, the main anion is HCO_3^-, and the concentrations of Cd(II), Cu(II), Pb(II), Zn(II) are low. Over the course of the experiment, the pH of water varied between 7.5 and 8.6. Chemical-thermodynamic modeling (MINTEQ software [22]) of the metal's speciation in water of such composition showed that the introduction of additional Cu(II), Pb(II), and Zn(II) is accompanied by the formation and sedimentation of solid phases (carbonates and oxides). To avoid this, the natural water in the minicosms was acidified with HCl to pH 5.9 and 6.9 in the first and second experiments, respectively.

Three identical minicosm bags, each with a diameter of 1 m and a height of 1.5 m, were made from a 0.2-mm-thick transparent polyethylene film. Each bag was filled with 200 L of natural water, and the minicosm's contents were isolated from the external water. In the first experiment, solutions of $Cd(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ were added to each minicosm with the initial concentrations of the Cd(II), Cu(II), Pb(II), and Zn(II) at 0.2, 1.0, 1.0 and 2.0 mg/L of water, respectively, at pH of

5.9±0.1. Only solutions of Cd(II) and Zn(II) were added to the minicosms in the second experiment at a pH of 6.9±0.1. One minicosm was a control, and a 60×60-cm matrix with MC-HA5 was placed in the other two minicosms. After 4 days of the experiment, the matrices with sorbents were removed and treated with 0.05 M HNO_3 to desorb the metals, washed with natural water, and again placed in minicosms, where the metal concentrations were adjusted to the initial level. Such cycles were repeated three times for the first experiment and twice for the second experiment. Over the course of the experiment, water samples were taken for the analysis of the residual metal concentration in the water.

2.7 Data Analysis and Error Functions

In this study, two models were applied to investigate the kinetics of metal adsorption onto the hybrid adsorbents MC-HA5 and MC-HA15: pseudo-first-order (Eq. 2, [28]) and pseudo-second-order (Eq. 3, [29])

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{3}$$

where q_e and q_t are the sorption capacities in mg/g at equilibrium and at time t, respectively; k_1 is the rate constant of the pseudo-first-order sorption in L/min; and k_2 is the rate constant of the pseudo-second-order sorption in g/mg/min.

The classical models of Langmuir (Eq. 4, [30]) and Freundlich (Eq. 5, [31]) were used to describe the equilibrium sorption isotherms as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$q_e = K_F (C_e)^{\frac{1}{n}} \tag{5}$$

where q_m is the maximum sorption capacity in mg/g; K_L is the Langmuir constant (L/mg), which is related to the energy of adsorption; and K_F (mg/g)(L/mg)$^{1/n}$ and n are the Freundlich constants.

Table 1. Water chemistry

Ca^{2+}, mg/L	Mg^{2+}, mg/L	Na^+, mg/L	K^+, mg/L	HCO_3^-, mg/L	SO_4^{2-}, mg/L	Cl^-, mg/L	NO_3^-, mg/L	Zn, µg/L	Cu, µg/L	Cd, µg/L	Pb, µg/L
18.7	5.6	4.8	0.2	91.5	8.3	2.5	0.6	23	5	0.16	1.2

In the past, linear regression was frequently used to calculate or predict the isotherm/kinetic parameters or the most-fitted models by transforming the equations (2-5) into a conventional linear form. However, this approach can be limited, as it has an inherent bias resulting from the linearization approach; such data transformations implicitly alter the error structure and may result in a violation of the error equality of variance and the normality hypotheses for standard least squares [32-36]. Therefore, nonlinear forms of the kinetics and isotherm models (Eqs. 2-5) with error analyses and optimization techniques were employed in this study using the solver add-in in Microsoft excel 2010 program [34]. The error functions were:

- the coefficient of determination (r^2)

$$r^2 = \frac{\Sigma(q_{e,calc} - q_{e,av.})^2}{\Sigma(q_{e,calc} - q_{e,av.})^2 + \Sigma(q_{e,calc} - q_{e,\exp})^2}$$

(6),

- the root mean square error (RMSE)

$$RMSE = \sqrt{\frac{1}{m-p}\sum_{i=1}^{m}(qm - qe)^2}$$

(7),

- the Chi-square test (χ^2)

$$\chi^2 = \sum_{i=1}^{n}\frac{(q_{e,\exp} - q_{e,calc})^2}{q_{e,\exp}}$$

(8)

where:

- $q_{e,calc}$ is the equilibrium capacity obtained from the isotherm model.
- $q_{e,exp}$ is the equilibrium capacity obtained experimentally.
- $q_{e,av}$ is the average.
- $q_{e,exp}$, qe, and qm are the measured and modeled amounts of metal ion adsorbed
- at time t, respectively.
- m is the number of data points evaluated.
- p is the number of parameters in the regression model.

Smaller values of the error parameters (*RMSE* and χ^2) and higher r^2 value indicates a better fit between the model and the experimental data.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Sorbents

Table 2 shows the main characteristics of the HAs before and after oxidation with 5% or 15% hydrogen peroxide (HA, HA5 and HA15, respectively). The content of many elements such as Si, Ca, Mg, Na, and P significantly decreased after the oxidation of the initial HA in the presence of 1 M HCl; the Fe content decreased to a lesser extent. This explains the increase in the oxygen content in HA5 and HA15 compared to the initial HA. It can be assumed that in the binding of Cd, Cu, Pb, and Zn, the role of O-containing functional groups will be greater for HA5 and HA15, while the competition of other cations (Ca, Mg, Na) will, in contrast, be lower relative to the initial HA. The content of the elements of interest (Cd, Cu, Pb and Zn) was very low in all the samples. The specific surface area and total pore volume of HA5 and HA15 remained practically unchanged after oxidation of the initial HA.

General and SEM images of the initial polymeric matrix (a, c) and matrix with fixed MC-HA5 after five cycles of sorption-desorption of metals (b, d).

The FTIR spectra (Fig. 2) show the presence of many functional groups in the structures of the initial HA [37,38]. The intensity of the bands in the 1720–1710 cm^{-1} range corresponds to the valence vibrations of the C=O bonds of carboxyl groups; in the 1630-1620 cm^{-1} range, the carbonyl groups of the primary amides and the conjugate C=C bonds; at 1260 cm^{-1}, the C–O bonds of carboxylic acids and complex esters and the O–H bonds of phenols and carboxyl groups; in the 1100–1030 cm^{-1} range, the increased number of C–O bonds of alcohols and esters in HA5 and HA15 compared to HA. Thus, FTIR spectral analysis shows that the oxidation of the initial HA with H_2O_2 led to an increase in the content of SFGs that are capable of binding metals.

3.2 Surface Acid-base Groups

The characteristics of SFGs obtained by processing the pH-metric titration of MC-HA, MC-HA5, and MC-HA15 using the program ProtoFit 2.1 are presented in Table 3. Five species of acid-base SFGs differing in the values of constants were identified in all the adsorbents. Two species (pK_a = 3.76-5.45) may be assigned to carboxyl groups in aliphatic chains, species with a pK_a near 6.85 may be assigned to carboxyl groups in the aromatic ring or to N containing ionizable sites, and the species with a higher pK_a may be assigned to amine and phenolic groups, respectively [23,25]. The total concentration of SFGs in MC-HA (1.24 mM/g) increased up to 1.74 mM/g in MC-HA5 and to 1.80 mM/g in MC-HA15, mainly due to species with pK_a = 6.85. Clearly, this effect was the result of the oxidation of the initial HA with hydrogen peroxide. Taking into account the pK_a values of SFGs, it can be expected that the proportion of ionized samples will progressively increase with an increase in pH from 4 to 8, and, conversely, it will drop sharply at pH < 4. If these acid-base SFGs are binding metal cations, the sorption capacity of the investigated adsorbents for Cd(II), Cu(II), Pb(II), and Zn(II) should depend substantially on the water pH. Due to the higher concentration of SFGs in MC-HA5 and MC-HA15, their adsorption capacity may be higher than that of MC-HA.

3.3 Adsorption Capacity

The adsorption capacity of the hybrid adsorbents for Pb(II), Cu(II), Zn(II), and Cd(II) was studied in equilibrium batch experiments at different pH values. The uptake of all the metals increased with increasing pH and was higher for MC-HA5 and MC-HA15 than for MC-HA (Table 4). This is consistent with the assumption (Section 3.2) of an increase in the number of different acid-base SFGs involved in the binding of metals as the pH increases from 5 to 8. The higher adsorption capacities of MC-HA5 and MC-HA15 are the result of a corresponding increase in the SFGs concentration in comparison to MC-HA (Table 3) and not with other properties, such as the specific surface area and total pore volume, which are approximately the same for all adsorbents (Table 2).

To assess the role of the nature of the metals in binding to the SFGs, one must compare the sorption capacity (mmol/g) for all the metals at a single pH. At a pH of 6, the adsorption capacity as a function of the metal cation is ordered as Cu(II) > Pb(II) > Zn(II) > Cd(II) (Table 4). Abate and Masini [23] reported a similar order (Cu(II) > Pb(II) > Cd(II) ≈ Zn(II)) for the average stability constants for metal complexation by HAs isolated from river sediments. The observed agreement may be an additional argument in favor of this mechanism of binding metal with HAs in hybrid sorbents in this study.

Since the sorption of all the metals was higher for the hybrid adsorbents containing oxidized HA, subsequent kinetic and isothermal studies were conducted for MC-HA5 and MC-HA15.

The uptake of Cd(II), Cu(II), Pb(II), and Zn(II) by MC-HA5 and MC-HA15 at optimal conditions was higher than or at least equal to that of activated carbon, natural materials (lignin and combined biosorbent), and hybrid adsorbents containing HA (Table 5). Therefore, both of the hybrid adsorbents obtained are good candidates for removing these metals from metal-containing effluents.

3.4 Kinetic Studies

Kinetic experiments were carried out for the following time intervals: 5, 10, 15, 20, 25, 30, 40, 60, 90, 120 and 180 min.; the experiments used suspensions of fine particles of MC-HA5 and MC-HA15 at pH 6.0. The rate of metals uptake was very fast within the first 10 min., and the process reached the equilibrium state within 60 min. of the contact time in all cases (Fig. 3). A fast initial stage of sorption is associated with the presence of a large number of readily available binding sites, and the gradual occupation of the sites leads to a decrease in the rate of sorption in the second stage. The metal ion loadings after 60 min. were higher for MC-HA15 than for MC-HA5, which could be associated with the higher SFG content on MC-HA15 (Table 3). As seen in Fig. 3, both kinetic models (pseudo-first-order and pseudo-second-order) can be used to characterize the kinetics of metal ion sorption. The parameters of these models (Eqs. 2 and 3, respectively) and their respective error functions are presented in Table 6. The values of the coefficient of determination r^2 are high (>0.9975) and close for both models for all cases. An evaluation of the two error parameters (*RMSE* and χ^2) shows that the pseudo-second-order model better describes the experimental data than the pseudo-first-order model. From this, it can be concluded that the rate-controlling mechanism for the adsorption of metal ions onto

adsorbents is chemisorption. However, the closeness of the parameters obtained from both models for the sorption of all the ions onto MC-HA5 and MC-HA15 indicates that chemical interactions between the ions in the adsorbate solution and the adsorbent may still influence sorption kinetics, but this may depend on the rate of diffusion. The results obtained in this study are similar to those reported by Asuquo et al. [36] on the kinetics of Cd(II) and Pb(II) sorption using a mesoporous activated carbon adsorbent. In general, the kinetic study showed that the sorption of all the metals was slightly higher onto MC-HA15 than MC-HA5, but the sorption mechanism was similar for both adsorbents.

3.5 Adsorption Isotherms

To obtain the experimental isotherms for adsorption of Cd(II), Cu(II), Pb(II), and Zn(II) onto MC-HA5 and MC-HA15, the equilibrium adsorption experiments were carried out at pH 6.0. The experimental data were analyzed with the Langmuir and Freundlich nonlinear models (Eqs. 4 and 5, respectively). A comparison of the experimental and model isotherms is shown in Fig. 4. The initial parts of the experimental isotherm are steep, and the equilibrium plateau is reached at low concentrations. An examination of Fig. 4 indicates that the Langmuir isotherm fits the experimental sorption data better than the Freundlich model for all the metals. The isotherm parameters and their respective error functions are presented in Table 7. The values of r^2 are higher, and the values of the two error parameters ($RMSE$ and χ^2) are much lower for the Langmuir model than for the Freundlich model. Based on this, it could be that metal sorption by MC-HA5 and MC-HA15 is probably monolayer sorption (the Langmuir model) rather than heterogeneous surface sorption (the Freundlich model). The influence of the metal's nature on the adsorption isotherms requires further analysis.
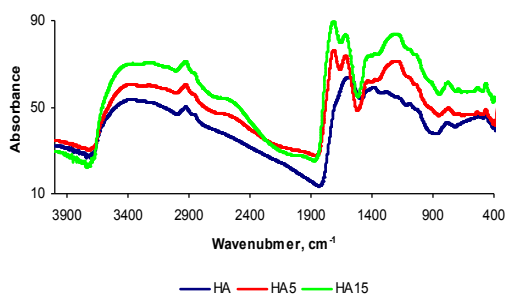

Fig. 2. FTIR spectra of HA, HA5 and HA15

3.6 Removal and Recovery of Metals from Model Wastewater

The above results show that the hybrid adsorbent MC-HA5, in the form of fine particles, have a good sorption ability for Cd(II), Cu(II), Pb(II), and Zn(II), and the adsorption process is fast and reaches equilibrium at low concentrations. However, the difficulty of solid–liquid separation limits the practical application of the adsorbent in simple submersible devices. To solve this problem, MC-HA5 was fixed to a high-porosity matrix. The obtained material was tested to evaluate the possibility of matrix reuse in the treatment of model wastewater. Fig. 5 shows the corresponding data on the removal and desorption percentages obtained from five consecutive adsorption–desorption cycles. The removal efficiency of metals was not less than 97.1% for Cd(II), 99.3% for Cu(II), 99.8% for Pb(II), and 96.1% for Zn(II). After sorption from a solution containing Cd(II), Cu(II), Pb(II), and Zn(II) at initial concentrations of 15, 30, 30, and 30 mg/L, respectively, the residual concentrations of Cd(II) (0.05–0.36 mg/L), Cu(II) (0.03-0.21 mg/L), Pb(II) (0.03-0.06 mg/L), and Zn(II) (0.15–0.54 mg/L) were less than the maximum permissible concentrations in wastewater (0.69, 3.38, 0.69 and 2.61 mg/L for Cd, Cu, Pb and Zn, respectively) [19]. Therefore, it can be assumed that hybrid adsorbents can be used in submersible devices for finishing sewage treatment. The efficiency of Cd(II) and Pb(II) desorption (95–100%) from the loaded sorbents was higher than that of Cu(II) (83.5–98%) and Zn(II) (83.7-88.4%). Probably, the reason for the higher desorption capacity of cadmium and zinc is associated with less binding of these metals with SFGs of adsorbents (see Sect. 3.3). It is important to note that the effectiveness of adsorption-desorption processes remains constant at least in five cycles, which confirms the good chemical stability of the hybrid sorbents. It can be concluded that the regeneration and subsequent use of humic-modified sorbents would be economically beneficial for practical applications.

3.7 Uptake of Metals from Contaminated Water Body

To evaluate the possibility of using hybrid adsorbents to remove metals from contaminated water bodies, field experiments were carried out. The conditions of the field experiment were substantially different from the previous laboratory experiment on model wastewater

treatment. Taking into account the large volumes of contaminated water bodies, the initial concentrations of metals were significantly less (0.2, 1.0, 1.0 and 2.0 mg/L for Cd(II), Cu(II), Pb(II), and Zn(II), respectively) and the dose of adsorbents was reduced to 0.6 g/L (instead of 6.7 g/L in the previous experiment). In addition, the field experiments were performed on a real water body, in a "passive" mode (that is, without additional mixing of the minicosm contents). The first experiment was carried out with the addition of all the metals at pH 5.9, and the second experiment was carried out with only the addition of Cd(II) and Zn(II) at pH 6.9.
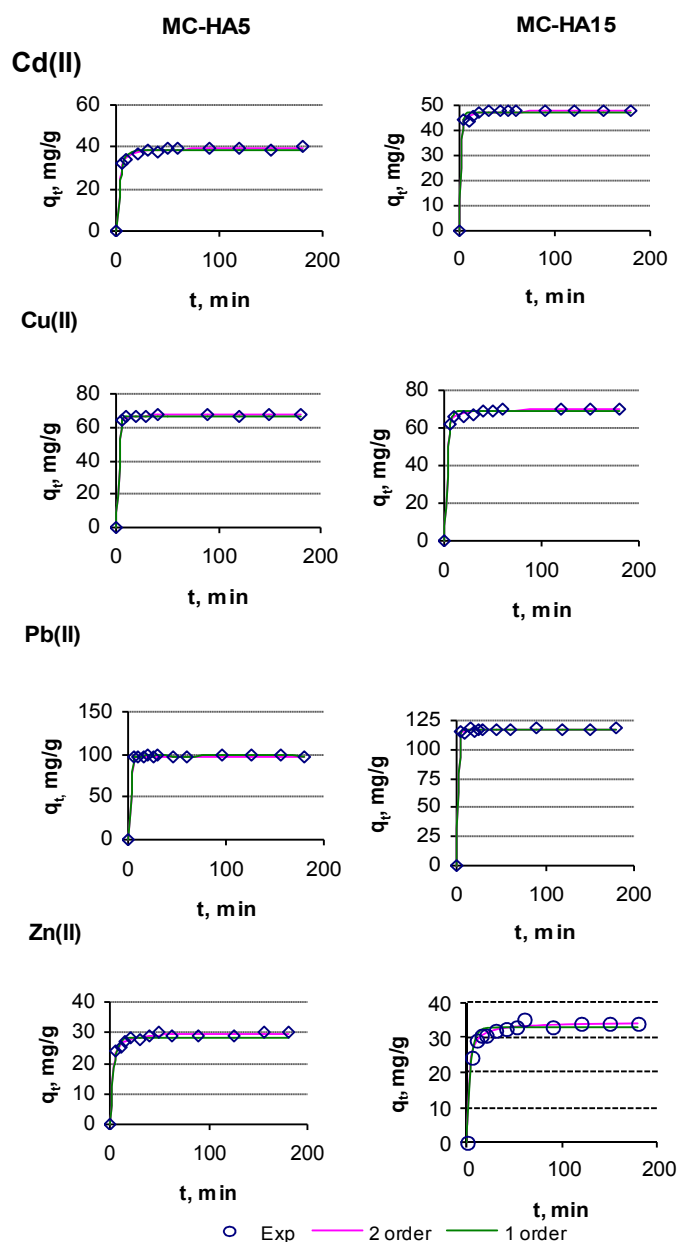

Fig. 3. Adsorption kinetics for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption onto MC-HA5 and MC-HA15; volume of solutions 100 mL; dose of adsorbent 0.05 g; shaking rate 200 rpm; pH 6, 20 C

Table 2. Composition, specific surface area (*A*), and total pore volume (*V_{por}*), of the humic acids

Material	Content, wt %															A, m^2/g	V_{por}, cm^3/g
	C	H	N	O*	S	Si	Ca	Mg	Fe	Na	P	Cd	Cu	Pb	Zn		
HA	54.3	4.4	0.8	28.7	<0.2	3.6	1.8	0.35	1.36	4.5	0.14	<0.0001	0.0002	0.005	0.006	10.0	0.01
HA5	55.1	4.2	0.7	38.8	<0.2	0.06	0.18	0.06	0.77	0.11	0.005	<0.0001	0.0001	0.0003	0.003	11.5	0.01
HA15	52.3	4.2	0.5	41.5	<0.2	0.07	0.29	0.07	0.83	0.20	0.009	<0.0001	0.0001	0.0009	0.002	12.8	0.01

* Content of O calculated by the difference between 100% and the amounts of the other elements

Table 3. Characteristics of SFGs in the hybrid adsorbents

MC-HA		MC-HA5		MC-HA15	
pK_a	*C* (mM/g)	*pK_a*	*C* (mM/g)	*pK_a*	*C* (mM/g)
4.08	0.298	3.93	0.191	3.76	0.234
5.45	0.233	5.34	0.275	5.27	0.398
6.84	0.204	6.85	0.436	6.86	0.650
8.24	0.250	8.08	0.407	8.59	0.257
9.56	0.250	9.66	0.436	9.28	0.257
Σ SFGs	**1.235**		**1.745**		**1.796**

Table 4. Sorption capacity of MC-HA, MC-HA5 and MC-HA15 towards Cd(II), Cu(II), Pb(II) and Zn(II) at different pH (numerator – mg g^{-1}, denominator – mmol g^{-1})

Sorbent	MC-HA				MC-HA5				MC-HA15			
pH	5	6	7	8	5	6	7	8	5	6	7	8
Cd(II)	18.4	22.1	27.2	43.2	24.4	39.0	49.8	65.4	32.0	42.4	51.2	69.8
	0.164	0.197	0.242	0.384	0.217	0.347	0.443	0.582	0.285	0.377	0.456	0.621
Cu(II)	38.8	53.2	-	-	48.0	62.8	-	-	53.4	65.5	-	-
	0.611	0.837			0.755	0.988			0.84	1.031		
Pb(II)	87.8	107.5	-	-	93.9	126.6	-	-	101.8	136.6	-	-
	0.424	0.519			0.453	0.611			0.491	0.656		
Zn(II)	18.4	24.4	29.0	-	19.4	26.9	35.2	-	27.2	30.2	36.6	-
	0.281	0.373	0.444		0.297	0.412	0.538		0.416	0.462	0.56	

Table 5. Sorption capacity (mg/g) of metals on different adsorbents

Sorbent material	Cd(II)	Cu(II)	Pb(II)	Zn(II)	Reference
Lignin	25.4	23.5	89.5	10.9	[39]
Activated carbon	27.3	-	20.3	-	[36]
Combined biosorbent	41.5	39.5	94	27.2	[40]
Fe_3O_4/HA	18.3	22.4	14.8	-	[14]
Moss/MC-HA	53.1	26.1	-	48.6	[22]
MC-HA5	65.4	62.8	126.6	35.2	Present study
MC-HA15	69.8	65.5	136.6	36.6	Present study

Table 6. Kinetic parameters for Cd(II), Cu(II), Pb(II), and Zn(II) adsorption on MC-HA5 and MC-HA15 at pH = 6

Kinetic Models	Parameter	MC-HA5	MC-HA15	MC-HA5	MC-HA15	MC-HA5	MC-HA15	MC-HA5	MC-HA15
		Cd(II)		Cu(II)		Pb(II)		Zn(II)	
Pseudo-first-order	$q_{e\,cal}$ (mg g^{-1})	38.42	47.17	66.93	68.81	97.86	116.83	28.38	33.02
	K_1 (min^{-1})	0.284	0.550	0.609	0.453	0.789	0.800	0.274	0.241
	r^2	0.9975	0.9994	1.000	0.9996	1.000	1.000	0.9987	0.9985
	RMSE	2.068	1.268	0.517	1.534	1.003	1.189	1.091	1.341
	χ^2	1.076	0.342	0.032	0.274	0.103	0.121	0.432	0.568
Pseudo-second-order	$q_{e\,cal}$ (mg g^{-1})	39.68	47.84	67.63	70.06	98.13	117.36	30.04	34.51
	K_2 (g mg^{-1} min^{-1})	0.020	0.047	0.053	0.021	0.082	0.065	0.020	0.014
	r^2	0.9996	0.9998	1.000	0.9999	1.000	0.9999	0.9994	0.9996
	RMSE	0.800	0.8	0.535	0.729	0.851	1.010	0.625	0.713
	χ^2	0.157	0.139	0.030	0.062	0.074	0.088	0.139	0.155

Table 7. Isotherm parameters for Cd(II), Cu(II), Pb(II), and Zn(II) adsorption on MC-HA5 and MC-HA15 at pH = 6

Isotherm models	Parameter	MC-HA5	MC-HA15	MC-HA5	MC-HA15	MC-HA5	MC-HA15	MC-HA5	MC-HA15
		Cd(II)		Cu(II)		Pb(II)		Zn(II)	
Langmuir	q_{max} (mg/g)	35.13	43.14	63.23	65.40	121.46	133.38	30.68	31.65
	K_L (L/mg)	2.038	2.414	2.014	1.541	4.171	1.375	0.758	0.582
	r^2	0.9959	0.9992	0.9944	0.9982	0.9979	0.9961	0.9970	0.9918
	RMSE	0.801	0.450	1.691	0.978	1.875	2.620	0.542	0.894
	x^2	0.177	0.042	0.811	1.203	0.830	1.631	0.097	0.507
Freundlich	K_F (mg/g)/(L/mg)$^{1/n}$	19.30	24.61	35.07	34.13	76.96	65.85	12.57	11.71
	$1/n$	0.221	0.222	0.294	0.318	0.257	0.346	0.331	0.359
	r^2	0.9394	0.9311	0.9734	0.9787	0.9658	0.9819	0.9841	0.9916
	RMSE	4.128	5.722	6.297	5.940	15.02	10.99	2.395	1.711
	x^2	7.383	11.65	12.41	10.49	36.26	19.01	3.487	1.934
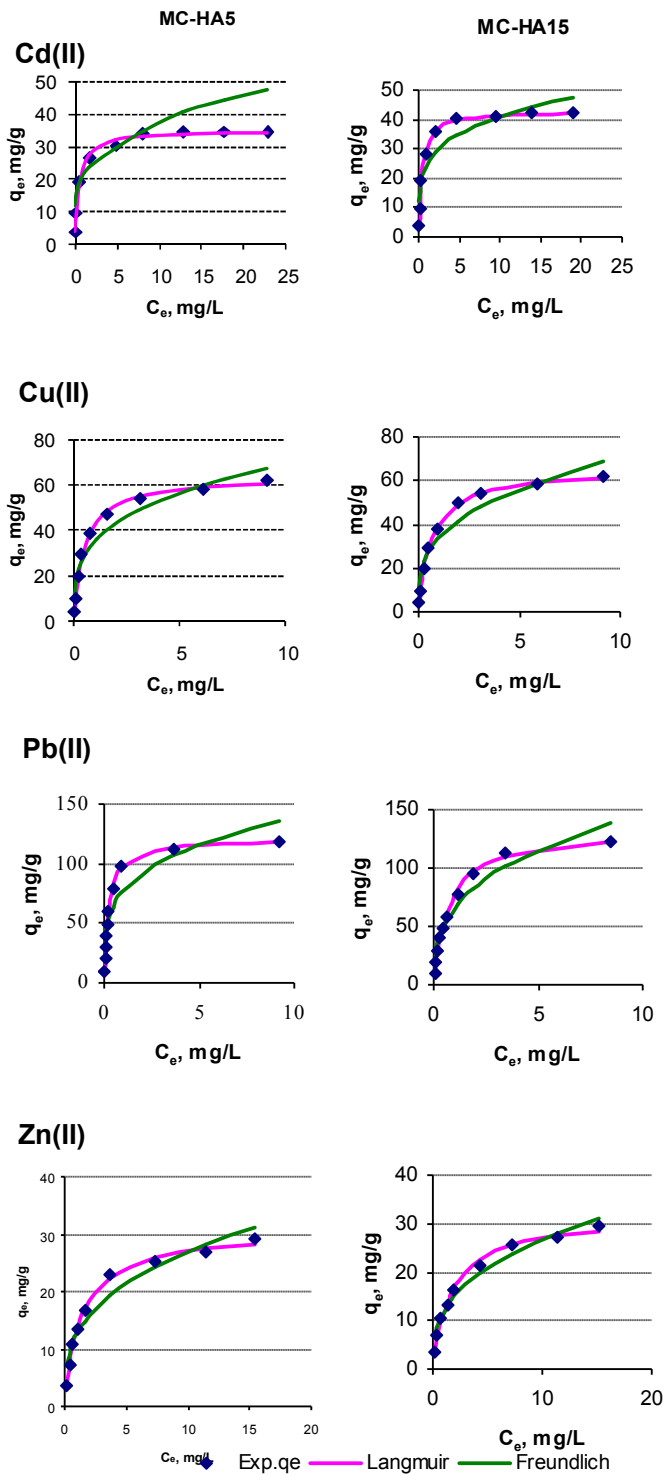
Fig. 4. Equilibrium isotherms for Cd(II), Cu(II), Pb(II) and Zn(II) adsorption onto MC-HA5 and MC-HA15; volume of solutions 100 mL; dose of adsorbent 0.05 g; shaking rate 200 rpm; pH 6, 20°C; equilibrium time 3h

(a)

(b)

■ Cd □ Cu ■ Pb ■ Zn
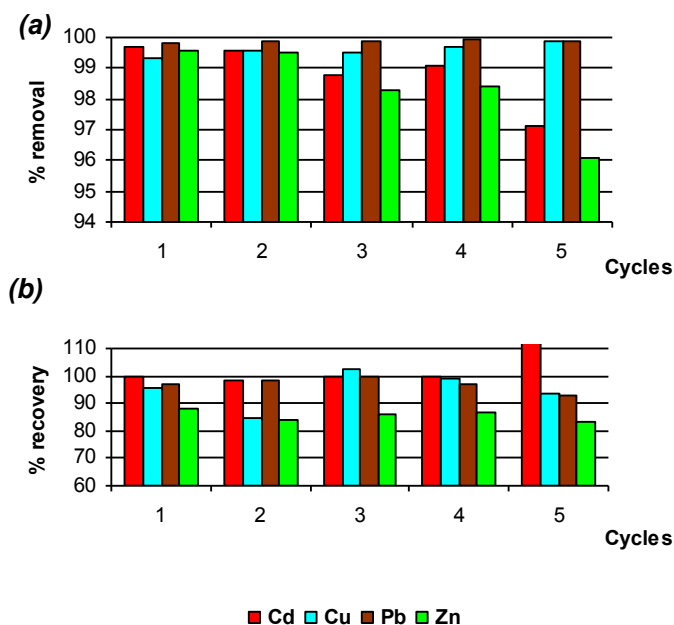
Fig. 5. Efficiency of metal's removal (*a*) and recovery (*b*) for MC-HA5 in 5 consecutive cycles. Removal: dose 1 g, 150 mL, initial concentration of Cd(II) 15 mg/L, Cu(II), Pb(II), and Zn(II) 30 mg/L of each, pH adjusted from 3.5 to 6.0; recovery: 150 mL of 0.05 M HNO₃; shaking rate 100 rpm, 20°C, equilibrium time 3h

The introduction of hybrid adsorbents into the minicosms resulted in a significant decrease in the residual concentration of Cu(II) and Pb(II) in the water after only 1 day (up to 10% relative to the initial level), compared with the control minicosm (Fig. 6). After 4 days, only 2% of Cu(II) and Pb(II) remained in the minicosm water containing MC-HA5. The rates of Cd(II) and Zn(II) removal were lower, and after 4 days their residual concentrations were 20 and 31% of their initial concentrations, respectively. Obviously, the observed difference in the removal efficiency of metals from water are directly related to the higher sorption capacity of MC-HA5 to Cu(II) and

Pb(II) than to Cd(II) and Zn(II) (Table 4). The trends of metal removal remained the same in subsequent cycles after the repeated introduction of the regenerated adsorbent at 5 and 10 days.

The removal efficiency for Cd(II) and Zn(II) was higher in the second experiment (Fig. 7) with a higher water pH (6.9 instead of 5.9), which can be explained by the increase in the Cd(II) and Zn(II) uptake at a higher pH. In this case, the residual concentration of Cd(II) and Zn(II) in water decreased to 10% and 20%, respectively, after 4 days.

a

b
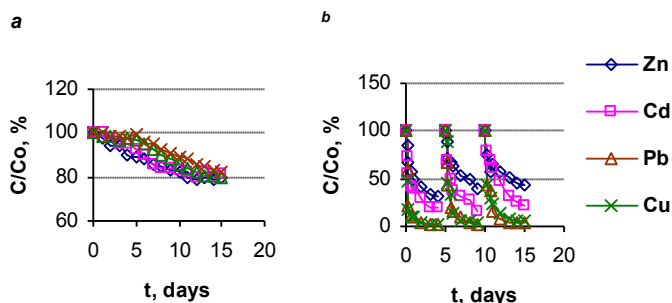
Fig. 6. Dynamics of residual concentrations of Cd(II), Cu(II), Pb(II) and Zn(II) in water at pH 5.9 in different minicosms: *a* - control, *b* - with addition of MC-HA5; re-introduction of metals and regenerated sorbent after 5 and 10 days

a   *b*
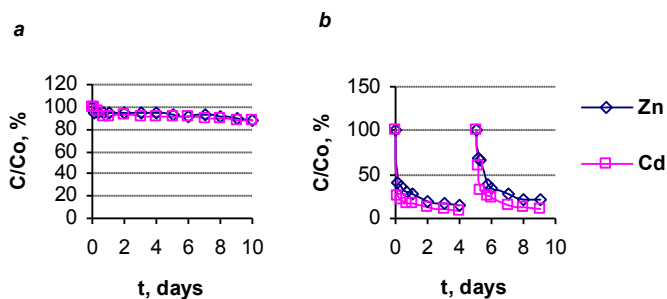
Fig. 7. Dynamics of residual concentrations of Zn(II) and Cd(II) in water at pH 6.9 in different minicosms: *a* - control, *b* - with addition of MC-HA5; re-introduction of metals and regenerated sorbent after 5 days

The results of the field experiment show that the material obtained by fixing the hybrid sorbent on a high-porosity matrix has the potential for reuse in the simplest "passive" submersible devices to remove metals from contaminated reservoirs.

4. CONCLUSION

In this study, hybrid adsorbents based on cheap materials (MC and HAs of natural origin) were obtained. The preliminary oxidation of HAs with H_2O_2 leads to an increase in the concentration of SFGs capable of binding metal cations (from 1.2 to 1.8 mmol/g) and, as a result, to an increase in the adsorption capacity of the hybrid adsorbents in the order Cd(II) < Zn(II) < Pb(II) < Cu(II). The adsorption process is fast and reaches equilibrium at low concentrations. The Langmuir isotherm fits the experimental sorption data better than the Freundlich model, indicating that the adsorption reaction for all the metals is a spontaneous chemisorption process. Fine particles of hybrid adsorbent were fixed onto a high-porosity polymeric matrix to produce a material suitable for practical reuse in simple submersible devices. The high efficiency of the adsorption-desorption processes is shown by the example of model multi-metal wastewater treatment using a porous matrix with the fixed adsorbent MC-HA5. The percentages of metal removal and desorption obtained from five consecutive adsorption–desorption cycles, were equal to 96.1-100% and 83.5-100%, respectively. In addition, the principle possibility of using a similar matrix in the simplest submersible device for removing metals from a contaminated reservoir is shown. Thus, the investigated hybrid adsorbents can be used for the treatment of large volumes of low-concentration wastewater and natural water contaminated with toxic metals.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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