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Zinc remediation of aqueous solutions by natural hemp fibers: batch desorption/regeneration study

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ABSTRACT

A hemp waste material resulting from the textile industry has previously been shown to be a very efficient material in removing Zn(II) from diluted aqueous solutions. In this work, batch studies on desorption and multiple sorption–regeneration cycles for zinc(II) removal by natural hemp fibers have been carried out. The best desorption results were performed in acidic medium, where the protons in solution replaced the Zn(II) ions on the loaded hemp. The efficiency of Zn(II) desorption with 0.1 M hydrochloric acid is higher than that achieved using sulfuric acid of the same concentration. The amount of Zn(II) desorbed by 0.1 M HCl, 0.1 M H_2SO_4, and 5% NaCl increases sharply in the first 15–20 min of the process, attaining values that subsequently stay almost constant (for 0.1 M HCl) or sligtly increase (for 0.1 M H_2SO_4 and 5% NaCl). The sorptive potential of the tested hemp remains almost unchanged after three cycles of sorption–desorption of Zn(II) from solutions with a high mg Zn/g of hemp in the initial ratio. The results of this study are important in order to demonstrate that regenerated hemp could be used for zinc metal removal from water sources without the threat of the sorbent becoming another source of zinc pollution for the environment.

Keywords: Desorption; Regeneration; Zinc; Hemp; Aqueous solution

1. Introduction

Both surface water and groundwater were reported to have been contaminated with heavy metal ions from natural and anthropogenic sources worldwide [1]. The heavy metals present in the aquatic environment are considered to be a major inorganic contaminants due to their mobility in the aqueous ecosystem, toxicity to higher life forms and nonbiodegradable nature [2]. There are various conventional treatment techniques available for the removal of heavy metals from groundwater, surface waters and wastewaters, such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, electrochemical treatment, membrane separation process, and adsorption [3,4]. Among these methods, adsorption has been found to be one of the most popular processes for the removal of heavy metals from aquatic environment due to its low complexity and straightforward implementation in field conditions as well as its potential regeneration

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capacity and sludge-free operation [5,6]. Increasing demand for eco-friendly techniques promotes the interest in natural and biodegradable sorbents. There are hundreds of studies regarding the equilibrium, kinetics, and thermodynamics of heavy metal ions sorption on a variety of natural materials and waste products [7–18].

The technological exploitation of the adsorption process for the removal of heavy metals depends on the efficiency of sorbent regeneration after metal desorption [19]. The used sorbents containing heavy metals can be disposed of either after the recovery of contaminants or without heavy metal recovery. In both cases, a secondary pollution appears because of the used sorbents and the chemicals used to treat the sorbents for metal recovery appears [1]. Still, metal-loaded sorbents have toxic effects on humans and environment. Thus, the process of adsorption can be economical and environment-friendly only if a suitable desorbing agent is used for the recovery of metals from the loaded sorbent. In a complete metal removal and recovery process, the sorbents must be used in a continuous sorption–desorption cycle [20]. For this purpose, the sorbents should meet the following criteria: (i) they should be cheap and reusable; (ii) both uptake and release of metal ions should be efficient and rapid; (iii) desorption of metal ions from the sorbents should be metal-selective and economically feasible [2].

The desorption/regeneration studies can help elucidate the mechanism of metal ion removal and provide insights useful for predicting the consequences of incorporating spent sorbents into the ecosystems and therefore are critical to the design of remediation strategies [21]. However, very few major studies have been published that deal with the recovery of metals sorbed from loaded sorbents [22–24].

Hemp is a fast growing plant in a variety of climates and soil types. It is naturally resistant to most pests, precluding the need for pesticides. The potential for hemp is vast, including sustainable biomass (power) and biodiesel (fuel). Our previous studies showed that hemp had good sorption abilities for heavy metals, so that its potential to be used in wastewater treatment was promising [25–35]. Thus, natural hemp fibers exhibited reasonable sorption properties for Zn(II) ions from aqueous solutions (the Langmuir maximum sorption capacity was determined as being 21.32 mg/g hemp) [36]. The sorption of Zn(II) ions by natural hemp fibers was highest at pH 5, increased with the hemp dose and the solution temperature and decreased with the increase in solution concentration [36].

Starting from these premises, the current study deals with the desorption process of zinc(II) from metal-loaded hemp, in order to provide data that could be beneficial in the paucity of literature information. Zinc(II) was chosen as cation in the study because, although an essential trace element for all forms of life, the excess of zinc in human body can cause a range of serious illnesses including anemia, damage to pancreas, lungs, decreased immune function, ranging from impaired neuropsychological functions to growth retardation and stunting, impaired reproduction, immune disorders, dermatitis, impaired wound healing, lethargy, loss of appetite, and loss of hair [37]. Beside its direct toxic effects, the bioaccumulation and biomagnification effects of Zinc(II) in aquatic organisms may indirectly affect humans.

2. Materials and methods

In these experiments, we used thick and rigid fibers of hemp with large surface area and porosity, high swelling capacity, and strong hydrophilic character. They resulted as waste from a textile factory. Hemp fibers were purified by having been boiled for 4 h in a solution containing soap and soda ash, then washed several times with water, and then rinsed with bidistilled water and dried in oven at 45°C.

Stock solution of 1,000 mg/L was prepared by the dissolution of analytical grade reagent $ZnSO_4 \cdot 7H_2O$, in deionized water and was complexonometrically standardized. Working solutions of Zn(II) were prepared by the appropriate dilutions of the stock solution.

2.1. Batch desorption studies

The experiments were performed in batch conditions and focused on the optimization of the Zn(II) desorption efficiency. The recovery of Zn(II) and the hemp reusability were assesessd by succesive cycles of Zn(II) sorption–desorption.

The batch desorption of Zn(II) from metal-loaded hemp was performed according to the 2-step procedure presented in Fig. 1. The conditions provided for Zn(II) sorption on hemp are systematized in Table 1.

In the desorption step, the following solutions were used: 0.1 M HCl; 0.1 M H_2SO_4; 5% NaCl; 10% NaCl.

2.2. Batch studies on hemp regeneration

Three succesive cycles of sorption and desorption of Zn(II) were carried out in batch systems. Experiments were carried out on: H1 samples of hemp (for sorption–samples of 0.5 g had been equilibrated for 24 h with 50 mL of Zn(II) solution of 26.15 mg/L concentration; for desorption–the samples (after filtration and washing) were contacted with 25 mL of

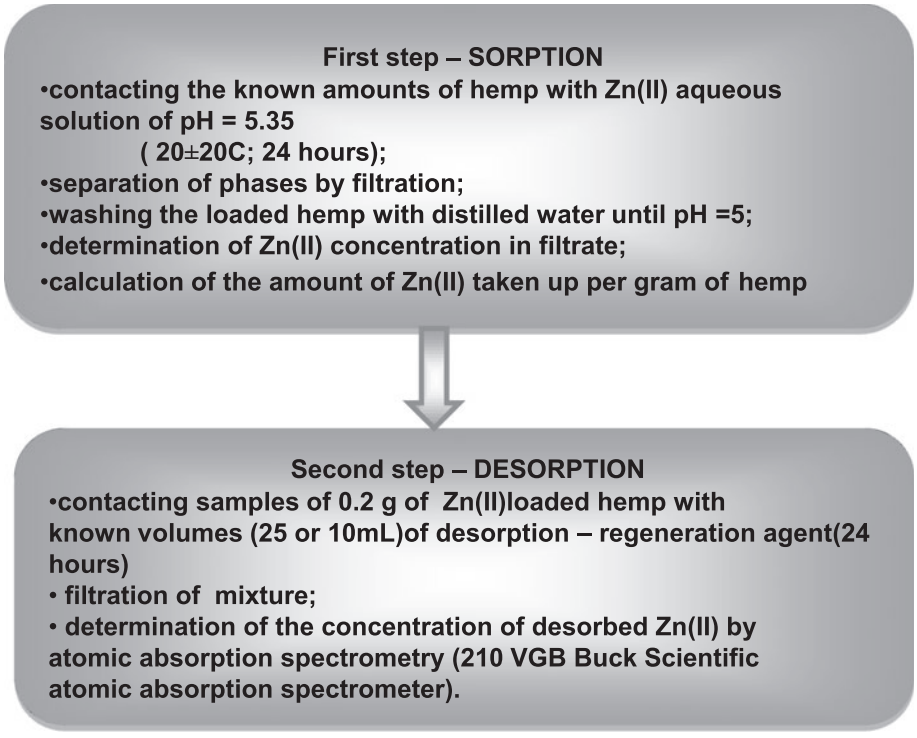

Fig. 1. Scheme of Zn(II) sorption–desorption in batch conditions.

Table 1
Preparing the samples of Zn(II)-loaded hemp for desorption

Sample	C_0, mg Zn(II)/L	Hemp dose, g/L	Initial ratio mg Zn(II)/g hemp	Amount of retained Zn(II) mg/g hemp	Retention percentage %	Used for
H1	26.15	10	2.61	3.92	100	Study on the influence of desorption time
H2	209.2	20	10.46	4.84	54.47	Succesive cycles of sorption–desorption
H3	52.3	4	13.07	7.12	46.27	

desorption agent), H2 samples of hemp (for sorption–samples of 1 g had been equilibrated for 24 h with 50 mL of Zn(II) solution of 209.2 mg/L concentration; similar conditions for desorption) and H3 hemp (similar conditions for sorption and desorption, but with the following differences: hemp samples of 0.2 g and the concentration of Zn(II) solution used for sorption was 52.3 mg/L).

3. Results and discussion

3.1. Desorption studies in batch conditions

3.1.1. Effect of the nature of the chemical agent used for desorption

A successful desorption process requires proper selection of the desorbing agents, which strongly depends on the type of sorbent and the mechanism of sorption. The chemical agents used for desorption should be: nondestructive to the sorbent, cost-effective, eco-friendly, and efficient [38].

A number of studies have been carried out on the desorption of zinc from sorbents using 0.1 M solutions of various acids (hydrochloric, sulfuric and nitric acids), salts, and complexing agents (ethylenediaminetetraacetic acid-EDTA) (Table 2). The reported superiority of EDTA in desorbing heavy metal ions from the metal ion laden sorbents is due to its ability to form stable complexes with metal ions and to reduce the solubility of metal ions in aqueous solution [45]. However, EDTA cannot be used for metal desorption in a commercial process, as it is more costly than HCl; moreover its disposal may cause serious environmental problems [46].

The high concentration on metal effluent, undiminished metal uptake on reuse, least physicochemical damage to sorbents, and the low cost exhibited by HCl show that it can be preferably used as agent of desorption and regeneration of the spent sorbents (Table 2).

The experimental results regarding the influence of the nature of the chemical agent used on the desorption process of Zn(II) ions from different samples of metal ion-loaded hemp are depicted in Figs. 2 and 3.

According to Figs. 2 and 3, the best results are performed in acidic medium, where the protons in solution replace the Zn(II) ions on the loaded hemp. On the other hand, it is obvious from Figs. 2 and 3 that the increase in the metal ion amount loaded by hemp resulted in a decrease in the desorption percentages achieved with all desorbing agents under study.

The high efficiency of Zn(II) desorption is achieved with 0.1 M hydrochloric acid. This behavior may be due to the capacity of Zn(II) ions to form complexes with chloride anions.According to findings from other works, it may be considered that in the case of HCl use as desorbing agent, the sorbent surface is completely covered with H^+ ions, while the coordination sphere of chelated ions is disrupted [36]. Under these conditions, Zn(II) ions cannot compete with protons for the sorption sites and, consequently, the Zn(II) ions are released from the sorbent surface into the solution. At the end of the desorption process, the sorbent becomes completely protonated, ready for the next sorption cycle.

The efficiency of Zn(II) desorption with 0.1 M sulfuric acid is lower than that achieved using hydrochloric acid of the same concentration. The poor desorption ability of sulfuric acid might be correlated with the strength of the acids. Thus, hydrochloric acid has the highest acid strength ($pK_a = -6.3$) followed by sulfuric acid ($pK_a = -3$) [47]. This explanation is in close agreement with literature data which reported a general trend of decrease in the extent of metal desorption with decrease in the strength of acids [48]. It

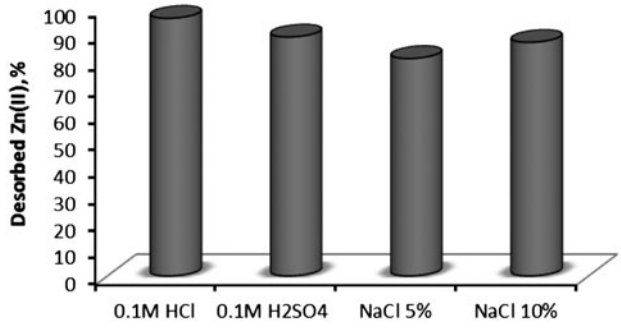

Fig. 2. Zn(II) desorption from H2 hemp (loaded with 4.84 mgZn/g): volume of desorption agent solution = 25 mL.

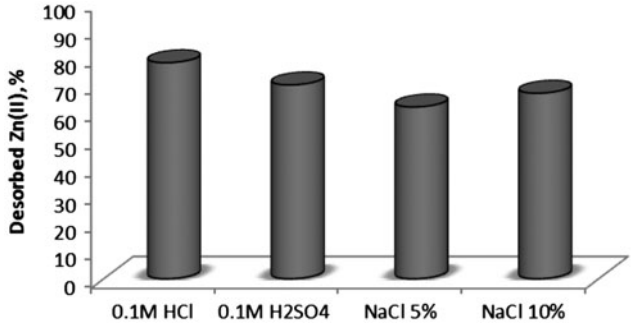

Fig. 3. Zn(II) desorption from H3 hemp (loaded with 7.12 mg/g); 25 mL of desorption agent.

Table 2
Comparison of the efficiency of different agents in zinc desorption from some low-cost sorbents

Low-cost sorbent	Desorption agent	Percentage of zinc desorption	Number of desorption cycles	Reference
Alginate beads	0.1 M HCl 0.1 M H_2SO_4	90–100%		[39]
Crab shell particles	0.1 M HCl	>99%		[40]
Immobilized *Candida utilis* and *Candida tropicalis* cells	0.1 M HCl	>95%		[41]
Lagenaria vulgaris shell	0.1 M HNO_3	96–93%	6	[42]
Arrabaena variabilis	0.1 M EDTA	93–85%	5	[43]
A. variabilis immobilized in calcium alginate matrix	0.1 M EDTA	91–82%	5	[43]
A. variabilis immobilized in agar matrix	0.1 M EDTA	88–84%	5	[43]
Sargassum filipendula biomass	0.1 M H_2SO_4 0.1 M $MgSO_4$	>90%	10	[44]

has been reported in the literature the possible mechanisms and conditions of desorption by acids, as follows: (1) low pH favors desorption and/or dissolution of metal cations, (2) strong competition between H^+ ions and metal cations for sorption sites causes displacement of cations into the acid solution, (3) acidic condition favors the release of adsorbed/surface-precipitated metals, and (4) acid reacts with residual alkalinity and lowers sorption capacity [49].

Due to their nontoxic properties and low cost, aqueous solutions of sodium chloride of two different concentrations were also tested to verify that all the metal ions present in the hemp could be desorbed (Figs. 3 and 4). It was found that the use of sodium chloride solution resulted in a little larger percentages desorption than mineral acid solutions. The increase in NaCl concentration (from 5 to 10%) has the effect of desorbed Zn(II) percentage increasing. Desorption results for NaCl solutions may be due to the formation of zinc ion stable complexes with chloride anions. The electrostatic repulsion between these zinc species and the functional groups of hemp can promote desorption.

3.1.2. Effect of contact time on Zn(II) desorption from hemp

Contact time is an important parameter for the economical value of the wastewater treatment process. Fig. 5 illustrates the variation of Zn(II) desorption from H1 samples of hemp (with a loading of 26.1 mg Zn(II)/g) by using 25 mL of 0.1 M HCl, 0.1 M H_2SO_4, and 5% NaCl, respectively, as function of contact time phases.

The plots in Fig. 4 point out that the desorption process is fast. The amount of Zn(II) desorbed by 0.1 M HCl, 0.1 M H_2SO_4, and 5% NaCl increases sharply in the first 15–20 min of the process, attaining values that subsequently stay almost constant (for 0.1 M HCl) or sligtly increase (for 0.1 M H_2SO_4 and 5% NaCl). A similar trend was observed in previous studies on the desorption of heavy metal ions from low cost sorbents [23,24,46]. This close agreement leads to the conclusion that it may be considered that the desorption process of zinc ions from hemp by acidic solutions comprises three steps: (1) desorption of metal ions from the binding sites of the sorbent; (2) difussion of metal ions inside the surface of the sorbent and (3) diffusion of metal ions across a stationary liquid film surrounding the sorbent and into the bulk film [46].

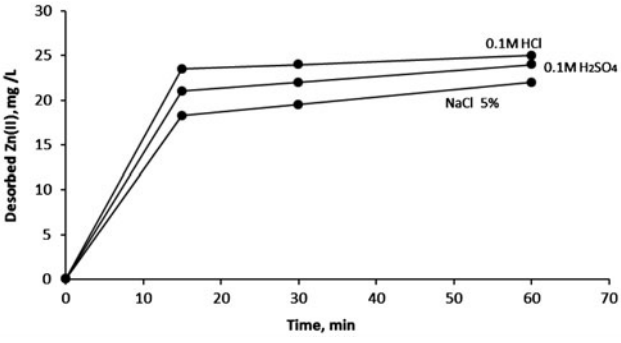

Fig. 4. Effect of desorption time on Zn(II) recovery from H1 hemp.

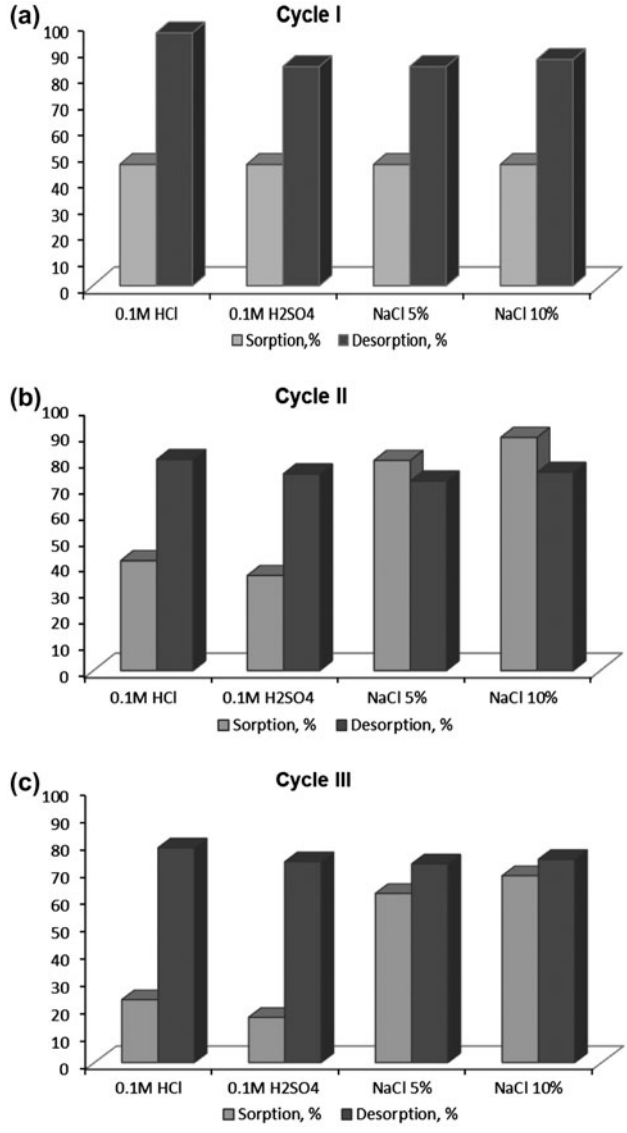

Fig. 5. Succesive cycles of Zn(II) sorption–desorption on H2 hemp (C_0 = 209.2 mg/L; 1 g hemp/50 mL).

3.2. Recovery of Zn(II) and hemp reusability in succesive cycles of Zn(II) sorption–desorption

A major step in the profitability of a sorption process is the sorbent regeneration. The zinc-loaded papaya wood was completely desorbed with 0.1 M HCl. During repeated biosorption–desorption for five cycles, no loss in the efficiency of zinc removal from their respective solutions and the zinc-loaded biomass was noted [50]. Another reusability studies indicated that the *Botrytis cinerea* biosorbent could be regenerated with up to 98% recovery of zinc and reused five times in sorption–desorption cycles successively [51].

To assess the reusability of the investigated wastes of hemp for Zn(II) removal from aqueous solutions, three succesive cycles of sorption and desorption of Zn(II) were carried out in batch systems. The experimental results are illustrated in Figs. 5 and 6.

The data obtained in Fig. 5 shows that the percentage of the Zn(II) desorbed from samples of 1 g of H2 hemp decreases significantly (from 99 to 785.% for 0.1 M HCl and from 86.2 to 74.32% for 10% NaCl, respectively) after three cycles of sorption–desorption. At the same time, it is worth noticing the considerable decrease in the capacity of Zn(II) sorption by hemp regenerated with acids (the sorption percentage decreases from 46.24% on original hemp to 22.95% on hemp regenerated two times). On the contrary, in the case of hemp samples desorbed and regenerated with solution of 5% NaCl and 10% NaCl, respectively, an increase in the Zn(II) sorption percentage takes place (the sorption percentage increases from 46.27% on original hemp to over 80% on regenerated hemp). The increase in concentration of the NaCl solution from 5 to 10% results in the increase of the Zn(II) sorption and desorption percentages.

The results of succesive cycles of sorption–desorption on H3 hemp (Fig. 6) can be described in a similar manner, except for the variation of the desorption percentages for all used agents whose range is narrower.

As compared with the previous case, the amount of Zn(II) retained on the original hemp is much higher and the desorption is not quantitative (below 80% for all used agents of desorption). There is a significant increase in the sorption capacity of the hemp regenerated with NaCl solutions as well as a decrease for hemp regenerated with mineral acids.

This behavior might be due to the acid strength of the desorbing agent. Therefore, mineral acids (hydrochloric acid and sulfuric acid) would cause more damage to sorbing sites or accessibility to the binding sites than sodium chloride as the cycles progressed [52].

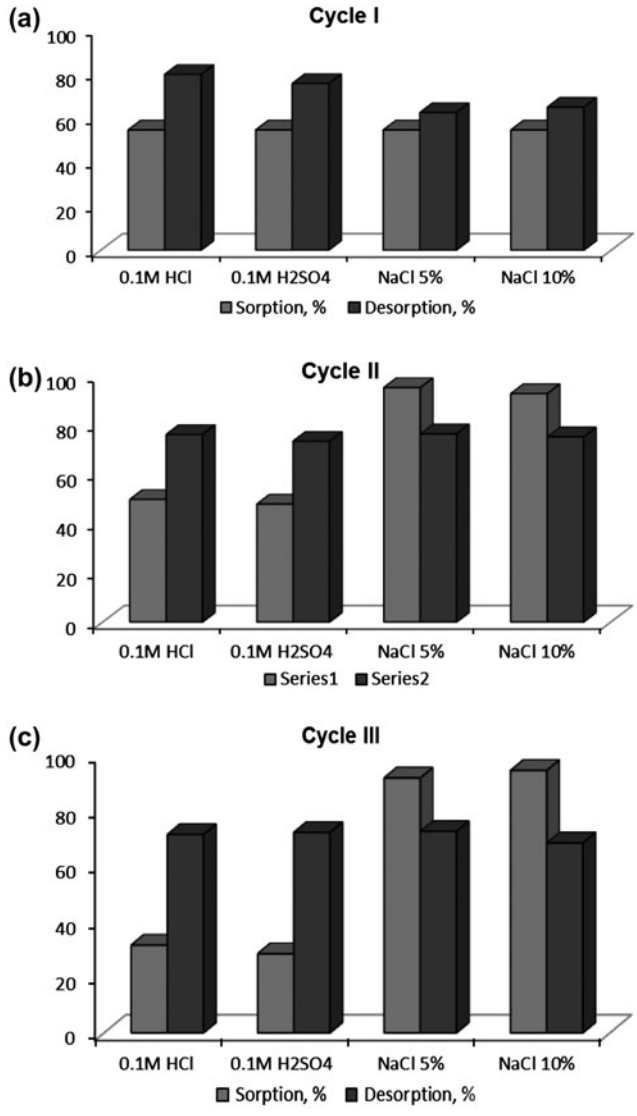

Fig. 6. Succesive cycles of Zn(II) sorption–desorption on H3 hemp (C_0 = 52.3.2 mg/L; 0.2 g of hemp/50 mL).

The morphological structure of Zn(II)-loaded hemp fibers and acid regenerated hemp was studied by scanning electron microscopy (Bruker AXS-Microanalyse GmbH microscope). Fig. 7 shows images of hemp loaded with Zn(II) ions (a) and regenerated hemp fiber (b). SEM images clearly show the morphological changes occurring on the surface of the hemp fiber after the Zn(II) sorption–desorption cycles as shown in Fig. 7.

The obtained results show that Zn(II) ions can significantly be recovered from the hemp after the sorption process before the material is ultimately disposed

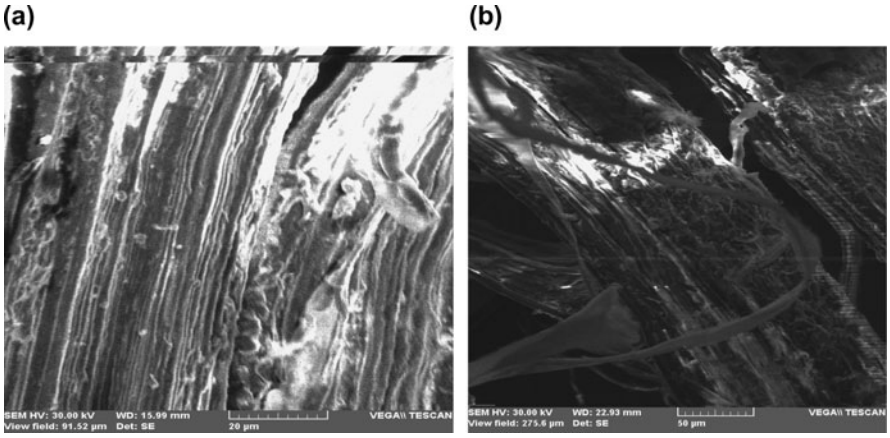

Fig. 7. SEM photographs of: (a) hemp fibers loaded with Zn(II) ions and (b) acid regenerated hemp fibers.

of into the environment. That is an important fact which proves that regenerated hemp could be used to removed zinc metal from water sources without the threat of the sorbent becoming another point source of zinc pollution for the environment.

4. Conclusions

The effects of the nature of the desorbing agent and the contact time on the Zn(II) recovery from metal ion-loaded hemp were studied. The results of batch studies show that high efficiency of Zn(II) desorption is achieved with 0.1 M hydrochloric acid. The relatively poor desorption ability of sulfuric acid was correlated with the strength of acids. The sodium chloride solution use resulted in a little larger percentages desorption than mineral acid solutions. The increase of NaCl concentration (from 5 to 10%) has the effect of desorbed Zn(II) percentage increasing. The desorption process of Zn(II) with 0.1 M HCl, 0.1 M H_2SO_4, and 5% NaCl is fast. On the basis of contact time influence, it can be considered that the desorption process of zinc ions from hemp by acidic solutions comprises three steps: desorption of metal ions from the binding sites of the sorbent→difussion of metal ions inside the surface of the sorbent→diffusion of metal ion across a stationary liquid film surrounding the sorbent and into the bulk film. To assess the reusability of the investigated wastes of hemp for Zn(II) removal from aqueous solutions, three succesive cycles of sorption and desorption of Zn(II) were carried out in batch systems. The percentage of the Zn(II) desorption from samples of 1 g of H2 hemp decreases significantly (from 99 to 785.% for 0.1 M HCl and from 86.2 to 74.32% for 10% NaCl, respectively) after three cycles of sorption–desorption. It should be noticed the significant increase in the sorption capacity of the hemp regenerated with NaCl solutions and also the decrease for hemp regenerated with mineral acids.

References

[1] Y. Tzou, S. Wang, L. Hsu, R. Chang, C. Lin, Deintercalation of Li/Al LDH and its application to recover adsorbed chromate from used adsorbent, J. Appl. Clay Sci. 37 (2007) 107–114.
[2] S.P. Mishra, Adsorption–desorption of heavy metal ions, Curr. Sci. 107 (2014) 601–612.
[3] F. Fung, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418.
[4] M.A. Barakat, New trends in removing heavy metals from industrial wastewater, Arab. J. Chem. 4 (2011) 361–377.
[5] M. Ahmaruzzaman, V.K. Gupta, Rice husk and its ash as low-cost adsorbents in water and wastewater treatment, Ind. Eng. Chem. Res. 50 (2011) 13589–13613.
[6] Y. Wu, Y. Wen, J. Zhou, J. Cao, Y. Jin, Comparative and competitive adsorption of Cr(VI), As(III) and Ni (II) onto coconut charcoal, Environ. Sci. Pollut. Res. 20 (2013) 2210–2219.
[7] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review: Bioresour. Technol. 99 (2008) 3935–3948.
[8] K.M. Shareef, Sorbents for contaminants uptake from aqueous solutions. Part 1: Heavy metals, World J. Agr. Sci. 5 (2009) 819–831.
[9] M.A. Hubbe, S.H. Hasan, J.J. Ducoste, Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals, BioRes. 6 (2011) 216-2287.
[10] V.C. Renge, S.V. Khedar, S.V. Pande, Removal of heavy metals from wastewater using low cost adsorbents: A review, Sci. Revs. Chem. Commun. 2 (2012) 580–586.
[11] D. Sud, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review, Bioresour. Technol. 99 (2008) 6017–6027.

[12] U. Farooq, J.A. Kozinski, M.A. Khan, M. Athar, Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature, Bioresour. Technol. 101 (2010) 5043–5053.
[13] K. Chojnacka, Biosorption and bioccumulation–the prospects for practical applications, Environ. Int. 36 (2013) 299–307.
[14] T.A.H. Nguyen, H.H. Ngo, W.S. Guo, J. Zhang, S. Liang, Q.Y. Yue, Q. Li, T.V. Nguyen, Applicability of agricultural waste and by–products for adsorptive removal of heavy metals from wastewater, Bioresour. Technol. 148 (2013) 574–585.
[15] W. Plazinski, Binding of heavy metals by algal biosorbents. Theoretical models of kinetics, equilibria and thermodynamics, Adv. Colloid Interface Sci. 197–198 (2013) 58–67.
[16] M. Ghaedi, N. Morallanejad, Removal of heavy metal ions from polluted waters by using of low–cost adsorbents: Review, J. Chem. Health Risk 3(1) (2013) 7–22.
[17] M.A. Hararah, F. Al-Nasir, T. El-Hasan, A.H. Al-Muhtaseb, Zinc adsorption–desorption isotherms: Possible effects on the calcereous vertisol soils from Jordan, Environ. Earth Sci. 65 (2012) 2079–2085.
[18] T. El-Hasan, Z. Al-Anbar, M. Batarseh, F. Al-Naser, M. Al-Anbar, A. Ziadat, Y. Kato, A. Jiries, Removal of Zn^{2+}, Cu^{2+} and Ni^{2+} ions from aqueous solutions via Tripoli: Simple component with single phase model, Curr. World Environ. 3(1) (2008) 1-14.
[19] S. Lata, P.K. Singh, S.R. Samadder, Regeneration of adsorbents and recovery of heavy metals: A review, Int. J. Environ. Sci. Technol. 12 (2015) 1461–1478.
[20] T. Mahmood, S.A. Malik, S.T. Hussain, Biosorption and recovery of heavy metals from aqueous solutions by *Eichhornica crassipes* (water hyacinth ash), BioRes. 5 (2010) 1244–1256.
[21] W.S. Wan Ngah, A. Kamari, Y.Y. Koay, Equilibrium and kinetic studies of adsorption of copper(II) on chitosan and chitosan/PVA beads, Int. J. Biol. Macromol. 34 (2004) 155–161.
[22] W.A. Stirck, J. van Staden, Desorption of cadmium and the reuse of brown seaweed derived products as biosorbents, Bot. Mar. 45 (2002) 9–16.
[23] D. Wankasi, M. Horsfall Jr., A.I. Spiff, Desorption of Pb(II) and Cu(II) from Nica palm (*Nypa fruticans Wurmb)* biomass, Afr. J. Biotechnol. 4 (2005) 923–927.
[24] M. Jr Horsfall, F.E. Ogban, E.E. Akporhonor, Recovery of lead and cadmium ions from metal–loading biomass of wild cocoyam using acidic, basic and neutral eluent solutions, Process. Biotech. 9 (2006) 1111–1116.
[25] L. Tofan, C. Păduraru, The hemp—A new fibrous natural unconventional sorbent, Bul. Inst. Polit. Iaşi XLVI (L) (2000) 113–118.
[26] C. Păduraru, L. Tofan, Equilibrium studies for the sorption of metal ions onto hemp, Cell. Chem. Technol. 36 (2002) 375–380.
[27] L. Tofan, C. Păduraru, I. Volf, Comparative study concerning the retention thermodynamics of some heavy metal ions on hemp fibers, Bul. Inst. Polit. Iaşi LVI (LX) (2010) 137–145.
[28] L. Tofan, C. Păduraru, I. Volf, C. Balan, Kinetic and thermodynamic profile of Pb(II) sorption by untreated hemp fibers, Scientific Papers Journal, Agronomy Series 53(1) (2010) 146–150.
[29] L. Tofan, C. Păduraru, I. Volf, C. Balan, Removal of lead (II) from aqueous solution by sorption on natural hemp fibers, Scientific Papers Journal, Agronomy Series 53 (2010) 150–153.
[30] L. Tofan, C. Teodosiu, C. Păduraru, R. Wenkert, Co(II) removal from aqueous solution by natural hemp fibers: batch and fixed–bed column studies, Appl. Surf. Sci. 285 (2013) 333–339.
[31] L. Tofan, C. Păduraru, Removal of copper (II) ions in traces from waste waters by sorption on hemp modified with α–benzoinoxime, J. Balkan Ecol. 2 (1999) 106–112.
[32] L. Tofan, O. Gherasim, C. Păduraru, O. Toma, Hemp impregnated with α-benzoinoxime for removal of copper (II) pollutant ions. Scientific Annals of Al. I. Cuza" University of Iaşi. Section II a. Genetics and Molecular Biology II (2001) 81–85.
[33] L. Tofan, C. Păduraru, O. Toma, Hemp fibers impregnated with alizarine S as unconventional material for Cr(III) ions in technological systems, Scientific Annals of the State University of Moldavia 1 (2001) 204–208.
[34] L. Tofan, C. Păduraru, Sorption studies of Ag (I), Cd (II) and Pb(II) ions on sulphdryl hemp fibers, Croat. Chem. Acta 77 (2004) 581–586.
[35] L. Tofan, C. Paduraru, I. Volf, Concentration of cadmium(II) trace amounts from large volumes of aqueous samples on chemically modified hemp fibers, Scientific Papers Journal, Agronomy Series 52 (2009) 506–511.
[36] C. Păduraru, L. Tofan, Investigations on the possibility of natural hemp fibers use for Zn (II) removal from wastewaters, Environ. Eng. Manag. J. 7 (2008) 687–693.
[37] G.J. Fosmire, Zinc toxicity, Am. J. Clin. Nutr. 51 (1990) 225–227.
[38] S. Syed, Recovery of gold from secondary sources–A review, Hydrometallurgy 115–116 (2012) 30–51.
[39] R.M. Silva, J.P. Manso, J.R. Rodrigues, R.J. Lagoa, A comparative study of alginate beads and an ion-exchange resin for the removal of heavy metals from a metal plating effluent, J. Environ. Sci. Health Part A 43 (2008) 1311–1317.
[40] K. Vijayaraghavan, H.Y.N. Winnie, R. Balasubramanian, Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions, Desalination 266 (2011) 195–200.
[41] M.F. Ahmad, S. Haydar, T.A. Quraishi, Enhancement of biosorption of zinc ions from aqueous solution by immobilized *Candida utilis* and *Candida tropicalis* cells, Int. Biodeterior. Biodegrad. 83 (2013) 119–128.
[42] D.L. Mitic-Stojanovic, D. Bojic, J. Mitrovic, T. Andjelkovic, M. Radovic, A. Bojic, Equilibrium and kinetic studies of Pb(II), Cd(II) and Zn(II) sorption by *Lagenaria vulgaris* shell, Chem. Ind. Chem. Eng. Q. 18 (2012) 563–576.
[43] N. Gaur, R. Dhankhar, Removal of Zn(II) ions from aqueous solution using *Arrabaena variabilis*: equilibrium and kinetic studies, Int. J. Environ. Res. 3 (2009) 605–616.
[44] A.A. Seolatto, M.M. Câmara, E.S. Cossich, C.R. Tavares, E.A. Silva, Zinc(II) desorption by *Sargassum filipendula* biomass in batch and in fixed–bed column for multiple sorption-regeneration cycles, Water Sci. Technol. 60 (2009) 357–362.

[45] Q.-Z. Li, L.-Y. Chan, J. Zhao, Z.-H. Yang, Q.-W. Wang, Lead desorption from modified spent grain, Trans. Nonferrous Met. Soc. China 19 (2009) 1371–1376.
[46] B. Sen Gupta, M. Curran, S. Hasan, T.K. Ghosh, Adsorption characteristics of Cu and Ni on Irish peat moss, J. Environ. Manage. 90 (2009) 954–960.
[47] J.W. Hill, R.H. Petrucci, General Chemistry, Prentice Hall, New Jersey, 1996.
[48] S. Srivastava, P. Goyal, Reusability of Biomaterial: A Cost-Effective Approach Novel Biomaterials, Springer, Berlin Heidelberg, 2010.
[49] Y. Zhou, R.J. Haynes, A comparison of inorganic solid wastes as adsorbents of heavy metal cations in aqueous solution and their capacity for desorption and regeneration, Water Air Soil Pollut. 218 (2011) 457–470.
[50] A. Saeed, M.W. Akhter, M. Iqbal, Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent, Sep. Purif. Technol. 45 (2005) 25–31.
[51] S. Tunali, T. Akar, Zn(II) biosorption properties of *Botrytis cinerea* biomass, J. Hazard. Mater. 131 (2006) 137–145.
[52] B. Volesky, Sorption and Biosorption, BV Sorbex Inc, St. Lambert, Québec, 2003.