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APPLICATION OF LOW-COST ADSORBENTS FOR COPPER REMOVAL FROM AQUATIC ENVIRONMENT

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Abstract

Waste water containing different types of heavy metal ions is being discharged from numerous sources and can cause several problems due to high toxicity and their solubility in the water. It is necessary to treat metal containing water before discharging into the environment. In recent years low-cost adsorbents are getting more and more popular. Their positives are low price, handling without further adjustment and in many cases these materials are based on waste or industrial by-products. On the other hand these simple materials exhibit worse sorption properties (specific surface area, sorption efficiency, etc.).

Sorption of Cu(II) ions from model solution and acid mine drainage onto four types adsorbents has been investigated. As sorptive materials peat, hemp shives, commercial adsorbent SLOVAKITE and silica were used. The best sorption properties showed modified version of silica (SBA – 15_DTAP) modified by N1-(3-Trimethoxysilylpropyl)diethylenetriamine with 46.3 mg/g of adsorption capacity. From the research also resulted the positive influence of NaOH modification of hemp shives on Cu(II) removal efficiency. Overall this study shows that low-cost adsorbents are able to compete with more expensive synthetically prepared adsorbents.

Key words

Acidic environment; heavy metals; low-cost adsorbents; sorption

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1 INTRODUCTION

The quality of water resources is deteriorating day by day due to the continuous addition of unfavourable chemicals in them. The main sources of water contamination are industrialization, agricultural activities and other environmental and global changes [1]. The contamination due to inorganic pollutants such as heavy metals is very dangerous due to their various side effects and toxicity. Therefore, the importance of water quality improvement is essential in life and increasing continuously. This improvement can be realized by conventional techniques for heavy metals removing from aqueous solutions, such as oxidation, reduction, filtration, ion exchange, reverse osmosis, chemical precipitation, electrolytic or liquid extraction, membrane techniques or biological processes. Many of these techniques, apart from being economically expensive, have several disadvantages like incomplete metal removal at low concentrations, high energy requirements and generation of toxic sludge or other waste by-products that require further disposal or deposition [2].

At present, there is growing interest in using low-cost materials and agricultural or industrial by-products for the adsorption of heavy metals. A wide variety of materials such as spent tea leaves [3], wheat bran [4], rice husk [5], fly ash [6], cellulosic materials [7], cactus leaves [8] sawdust [9], pine bark [10], walnut shells [11], animal bones [12] or holly oak [13] are being used as alternatives to expensive commercial industrial adsorbents. Predominant mechanism in this treatment process is ion exchange, but also there is surface adsorption, chemisorption, complexation or adsorption-complexation [14].

In presented paper, the study of Cu(II) sorption from model acidic solutions (pH ≈ 4) and acid mine drainage (AMD) is presented. Studied was removal efficiency of copper using different types of materials such as surface modified SBA – 15 silica, commercial adsorbent SLOVAKITE and low–cost adsorbents (peat, hemp shives). Results from experiments with model acidic solutions are compared with the behaviour of materials in the real samples of AMD, evaluated are also differences in sorption efficiencies of used adsorptive materials.

2 MATERIAL AND METHODS

2.1 Adsorbents

In this study four types of adsorbents were used. Two of them were low – cost natural materials and two types of synthetically prepared adsorbents. Low – cost sorbents include in this case natural non – modified peat “PEATSORB” (provided by REO AMOS; Slovakia) and hemp shives (provided by Hempflax; Netherlands). In experiments finer heterogeneous fraction of peat prepared by sieving through a 2 mm sieve was used.
The final fibre length of used technical hemp shives ranged between 4 mm and 0.063 mm. Hemp shives were used as natural and also modified [15]. Modification consisted in chemical treatment in order to gradually remove either hemicelluloses or lignin. The progressive removal of the hemicelluloses and keeping the lignin content unchanged was brought by treating the fiber samples with 1.6M NaOH solution, at room temperature (48 h contact time), followed by neutralisation with 1% acetic acid. Fibres were then washed with deionised water until the pH value was 7 [16].

As the first synthetic material, SBA – 15 silica and its two modifications were used. SBA - 15 (mesoporous silica), produced from 8 g of Pluronic P123 surfactant, 60 ml of water and 240 g of 2M HCl. After dissolution of the mixture 17 g tetraethoxysilane was added. The solution was stirred with a magnetic stirrer for 20 hours at 35 °C. Mixture was matured at 80 °C for 24 hours. The product was filtered off and allowed to dry at ambient room temperature. The resulting white powder was calcined at 500 °C for 7 hours. Modified samples were as follows:

- SBA – 15_AP – modified by (3-Aminopropyl)triethoxysilane
- SBA – 15_DTAP – modified by N1-(3-Trimethoxysilylpropyl)diethylenetriamine

The second synthetically prepared commercial material used in experiments was inorganic composite sorbent "SLOVAKITE" (provided by IPRES engineering; Slovakia). This commercial material, registered under Slovak patent no. 283214, uses a synergic effect of combination of natural sorption abilities of different types of materials (e.g. dolomite, tuffs, claystone, kaolin, sandstone, gypsum etc.).

All the adsorbents were dried at 105 °C for 2 h and then allowed to cool in the desiccators before using in experimental set-up.

2.2 Adsorbates

Synthetic solution of Cu(II) was prepared from analytical grade $CuSO_4.5H_2O$. Working solutions were prepared by further dilution to the initial concentration of 50 mg/L. The initial pH of each solution was adjusted to the required value (pH≈4) using sulphuric acid. It should be noted that sulphate anions are not forming precipitates or complexes with copper cations at the test conditions and are considered to be inert.

2.3 Apparatus and instrumentation

Concentrations of metal ions before and after the experiments were determined by colorimetric method using Colorimeter DR890 (HACH LANGE, Germany) with combination of appropriate reagent. pH values were determined by pH meter inoLab ph 730 (WTW, Germany) which was standardized using buffer solutions of different pH values (4.01, 7.00).

Specific surface area was estimated by low temperature gas adsorption using nitrogen gas (Quantachrome NOVA 1000e, USA) and subsequent application of Brunauer – Emmett – Teller isotherm.

2.4 Methodology

For the purpose of removal efficiencies investigation, batch adsorption experiments were carried out. The experiments were performed at laboratory temperature (23±0.2°C). The copper ion removal efficiency by sorptive materials was tested under static conditions. 1 g of sorbent (peat, hemp shives, SLOVAKITE) was mixed with 100 mL of model acidic solution containing 50 mg/L of copper cations. After 24 hours reaction time, sorbents were removed by filtration through a laboratory filter paper for qualitative analysis, residual concentration of copper was determined by colorimetric method and pH change was also measured. Due to the high sorption efficiency of the SBA – 15 silica samples, obtained from previous experiments, the batch rate was minimized to 0.1 g per 100 mL of model solution.

The second objective of this study was to treat AMD from Smolnik mine (Slovakia) and investigate the differences in sorbents behaviour caused by complex composition of AMD with comparison of synthetic samples. Before the sorption experiments AMD was modified due to high concentration of iron cations. Concentration of these cations is several times higher than the others and could distort the sorption. For this reason iron cations were removed by oxidation using 31% hydrogen peroxide and subsequent precipitation with 0.1 M sodium hydroxide. 100 mL of pretreated AMD was contacted with 1.0 g of each sorbent for 24 h. After the desired contact period the mixture was filtered and the filtrate was analysed.

As well as in experiments with model solutions the batch rate of SBA – 15 silica samples was minimized to 0.5 g per 100 mL of model solution.

2.5 Calculations

From experimental data the adsorption capacities were calculated by the following equation:

$$q = \frac{(C_0 - C_e)}{m} \; x V \;, \tag{1}$$

where C_o is the initial metal ion concentration (mg.L^{-1}), C_e the equilibrium metal ion concentration (mg.L^{-1}), V the volume of the aqueous phase (L), and m the amount of the adsorbent used (g).

The removal efficiencies (%) were calculated using the following equation:

$$\%\ Adsorption = \frac{(C_0 - C_e)}{C_0} \; x\, 100\,\% \tag{2}$$

3 RESULTS AND DISCUSSION

3.1 Specific surface area

Specific surface area (SSA) is one of the many properties which are used to characterize adsorbents. SSA plays important role in adsorption process; however as noted earlier there are other mechanisms that can influence the progress of adsorption, especially in the case of biosorption (e.g. ion-exchange abilities, chelation, complexation, ion entrapment in inter- and intrafibrillar capillaries and spaces of structural lignin and polysaccharide networks etc.). In order to evaluate the link between SSA and removal efficiencies estimation of SSA by physisorption of nitrogen gas at 77 K according to the BET method was carried out. The results are listed in *Tab. 1*.

Tab. 1: SSA of used adsorbents

	Peat	**Non – modified hemp**	**Treated hemp (NaOH)**	**Slovakite**	**SBA – 15**	**SBA – 15_AP**	**SBA – 15_DTAP**
SSA (m^2/g)	0.86	0.99	0.93	65.28	846	381	93

3.2 Model solutions – results

The results of sorption experiments with single – component solutions containing 50 mg/L of copper cations are presented in *Tab. 2*. From synthetically prepared adsorbents, the best sorption properties showed modified silica sample SBA – 15_DTAP. Slovakite showed also very god results relative to its precipitation abilities due to the increasing pH values (see *Tab. 3*). From low – cost natural materials, the sodium hydroxide modified hemp demonstrated the best sorption properties and it approaches adsorption capacity of slovakite.

Tab. 2: Final concentrations of copper and adsorption capacities; initial concentration 50 mg/L, initial pH≈4; 24 h contact time

Adsorbent	**Final concentration (mg/L)**	**Adsorption capacity (mg/g)**
Peat	13.75	3.63
Non – modified hemp	10.9	3.91

Treated hemp (NaOH)	5.55	4.45
Slovakite	0.15	4.99
SBA – 15	37	13
SBA – 15_AP	16.4	33.6
SBA – 15_DTAP	3.7	46.3

Data obtained from experiments in this study indicated that it is possible to improve sorption properties of natural sorbents by modification. Modification with sodium hydroxide (i.e. removal of hemicelluloses) resulted in improvement compared to non-modified samples. This can be explained by the domination of sorption at outer surfaces of fibers and increased the roughness of hemp fiber surfaces and induced new capillary spaces in inter-surfacial layer between completely or partially separated fibers due to the removal of lignin and hemicelluloses [2].

Tab. 3: pH values at the end of 24 h exposures; initial concentration 50 mg/L

	Peat	**Non – modified hemp**	**Treated hemp (NaOH)**	**Slovakite**	**SBA – 15**	**SBA – 15_AP**	**SBA – 15_DTAP**
pH	3.32	5.99	5.47	7.1	4.73	5.3	6

3.3 AMD removal efficiencies

Tab. 4 summarizes the result of Cu(II) removal from real sample of AMD. Initial concentration, results after iron oxidation and precipitation and results after sorption experiments are presented.

Modified silica sample SBA – 15_DTAP showed the best sorption properties overall and these results were achieved with a half dose compared to the other adsorbents. Modification by N1-(3-Trimethoxysilylpropyl)diethylenetriamine increased the efficiency by more than 70 % compared to the non – modified sample SBA – 15. These results were possibly achieved by support of precipitation, because SBA – 15_DTAP increased the pH value of more than 7. From low – cost adsorbents, the sodium hydroxide modified hemp was the most effective (same trend as in the experiments with synthetic solutions). Peat and non – modified hemp shives are almost on the same level.

Tab. 4: Results of sorption experiments on the real sample of AMD from Smolnik mine

	Concentration of metal (mg/L)		**Removal efficiency**	**pH**
	Fe_{total}	Cu(II)		
Input data	260	1.7	-	3.99
After iron oxidation and precipitation	0.62	1.66	-	3.80
After peat sorption	-	0.60	65.06	3.09
After non-modified hemp sorption	-	0.62	62.65	4.28
After treated hemp sorption	-	0.40	75.90	3.94
After Slovakite sorption	-	0.07	95.78	6.74
After SBA-15 sorption	-	1.26	24.09	3.53
After SBA-15_AP sorption	-	0.33	80.12	6.67
After SBA-15_DTAP sorption	-	0.03	98.19	7.65

4 CONCLUSIONS

This study showed the differences in sorption properties of the selected synthetically prepared adsorbents and low – cost adsorbents for copper removal from model acidic solutions and acid mine drainage. The best sorption properties showed modified version of silica (SBA – 15_DTAP) modified by N1-(3-Trimethoxysilylpropyl)diethylenetriamine with 46.3 mg/g of adsorption capacity, which is more than 10 – times higher compared to the other low – cost adsorbents used in this study. It was confirmed that NaOH modification of hemp shives has the positive influence on Cu(II) removal efficiency. Presented results affirmed suitability of low – cost adsorbents using for copper removal from acidic environment and their ability to compete with synthetically prepared adsorbents.

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