USING UNTRADITIONAL SORBENTS FOR SORPTION OF CERTAIN HEAVY METALS FROM WASTE WATER

SORPCE VYBRANÝCH TĚŽKÝCH KOVŮ Z ODPADNÍCH VOD POMOCÍ NETRADIČNÍCH SORPENTŮ

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Abstract

The environment incl. water is exposed to heavy metals in the long term. Typically, industrial activities are the source of heavy metals penetrating the environment. The heavy metals are contained in many products and are a part of many waste substances. This paper deals with removal of copper, zinc and lead from waste waters by means of adsorption. Adsorbents are typically cheap substances, such as synthetic zeolite, bentonite or slovakite. Attention is paid to the adsorption rate and efficiency of removal of the heavy metals mentioned from the water.

Abstrakt

Životní prostředí včetně vod je dlouhodobě zatěžováno těžkými kovy. Tyto se do prostředí dostávají hlavně činností průmyslu, jsou obsaženy v celé řadě výrobků a tvoří součást mnoha odpadních látek. Tento článek se zabývá odstraňováním mědi, zinku a olova z odpadních vod pomocí adsorbce. Jako adsorbenty jsou vybrány látky, které jsou cenově dostupné, Jedná se o syntetický zeolit, bentonit a slovakit. Je sledována rychlost adsorpce a účinnost odstraňování uvedených těžkých kovů z vody.

Key words: removal of heavy metals, adsorption, wastewater

1 INTRODUCTION

Utilisation of heavy metals and heavy metal compounds for various purposes in different industries results in accumulation of the heavy metals as hazardous and non-degradable wastes in the environment. Key sources producing the waste heavy metal are anthropogenic activities (mining and metallurgical plants), amortised products containing heavy metals, combustion of fossil fuel, traffic air pollutants, and excessive and/or incorrect application of pesticides and industrial fertilisers in agriculture. The heavy metals that have appeared in the environment through various exposure paths and are dissolved there pose a major threat for the health of all living organisms, including people.

Heavy metals rank among key contaminants that are subject to monitoring for all components of the living and natural environments. They occur in the open nature as compounds. They are hardly present as separate elements. They get into waters through various exposure paths (for instance, by bedrock infusion or wash-away). The presence of heavy metals is always regarded as foreign and hazardous, since the heavy metals result in serious illnesses and damage to organisms.

Elimination of heavy metals has been under investigation for a certain time, as certain technologies have proved to be little efficient or too costly. For those reasons more attention is paid now to utilisation of various natural materials or industrial wastes for heavy metal elimination technologies, because the natural materials and industrial wastes are less costly.

2 CHARACTERISTICS OF COPPER, ZINC AND LEAD

Dissolved copper and insoluble copper co-exist in natural wastes. Typically, copper enters the water from waste waters discharged from various industrial plants (see Table 1). In soil, the copper is present as copper ions with the Cr^{II} oxidising level and as complex compounds. Many compounds are mobile (mineral acid salts occurring as HNO_3, HCl). Stable Cu compounds include sulphides, oxides, phosphates and oxalic compounds. The concentration of copper ions in a soil solution is negligible. Most copper is bound to organic forms and creates water-soluble forms that sorbed to organic mass and inorganic materials, typically Fe and Mn oxides.

Copper is a biogenic element that is involved in enzymatic reactions in organisms. Excessive Cu is harmful to living organisms. Cu-compounds are toxic for fish and concentrations as low as 1 - 5 $mg.l^{-1}$ produce an unpleasant taste of water. Excess of copper damages intestinal flora and irritates mucous membranes in pharynx, stomach and bowels. It may accumulate in a liver or kidney and result in Wilson disease [1]. Carcinogenic, teratogenic or mutagenic effects of Cu and Cu-compounds have not been proved [2].

Lead ranks among the least mobile elements. The lead only occurs in high concentrations in ground water near lead ore pockets. Pb penetrates into water from corroded drinking water pipelines. The waste water from chemical industries and ore-processing plants takes the lead into surface waters (see Tab. 1). Lead from exhaust fumes enters surface water from the air. Lead typically enters organisms in food through digestion organs. Inhalation through air passages is less typical, but with high concentrations of lead in the air, this possibility exists too. The lead is difficult to secrete from organisms and deposits typically in bones. A long-lasting exposure to lead results in haematogenesis failures, indigestion and muscle disorders. Small children, once exposed, have been found to be underdeveloped and/or of lower intelligence. Carcinogenic effects have not been proved for the lead. Both dissolved and insoluble forms of lead are present in waters. The lead can be organically or inorganically bound.

Depending on pH and composition of water, lead is present as a dissolved Pb^{2+} cation or as various complex cations and/or anions. The lead also creates complexes with organic substances (for instance with humin acids). Therefore, it is caught by water infiltration through a soil horizon. It accumulates in a surface layer of soil, the concentration becoming lower towards depths.

Zink ranks among biogenic elements and is rather frequent in the nature, similarly to the copper. Zinc is present in structures of many minerals. It enters the ground water by infusion of sulphide ore. The zinc in surface water originates from waste water produced in metal surface treatment plants.

In soil, it is typically present as Zn^{2+}. Mobility of the ions is influenced mainly by the pH. In acid and neutral soils, Zn^{2+} occurs mostly, while in alkali soil the typical form is $Zn(OH)^{+}$. Migration capabilities of zinc in the soil are influenced considerably by the natural organic composition of the soil where as many as 80% of total zinc can be bound. The zinc is also easy to adsorb by hydrated clay Fe/Mn oxides that bind much of zinc-contaminated waters [3,4].

Tab. 1 Industrial processes that produce waste waters containing heavy metals and heavy metal compounds

Industrial processes	**Heavy metals present**
Ore mining and ore processing	Fe, Zn, Hg, As, Se, Mn, Cu
Metallurgy	Al, Cr, Mo, Ni, Pb
Coal mining	Fe, Al, Mn, Ni, Cu, Zn
Mechanical engineering, metal surface treatment	Cr, Cu, Ni, Zn, Cd, Fe, Al
Chemical industry	Fe, Al, W, Mo, Zn, Pb, Cu, Hg
Painting, varnishing, pigmenting	Hg, Cr, Pb, Zn. Ti, Al, Ba, Sr, Mn. As, Se
Pulp and paper	Ti, Zn, Al, Ba, Sr, Cr, Se, Cu, Hg
Leather processing	Cr, Al, Fe
Textile industry	Cu, Zn, Cr, Pb, Fe
Polygraphy	Zn, Cr, Ni, Cd, Pb
Electrical engineering	Ag, Se, Ge, Mn, Ni, Pb, Cu, Hg

Coal burning	As, Ti, Al, Ge, Se, Hg, Be, Zn, Mo, Ni, Pb, Sb
Heating oil burning	V, Ni, Zn, Cu
Pesticides	Hg, As, Cu, Zn, Ba
Industrial fertilisers	Cd, Mn, As
Pipe corrosion, inhibitors	Fe, Pb, Cu, Ni, Zn, Cr
Traffic (motor vehicles)	Pb

3 METHODS USED FOR CU ELIMINATION FROM WASTE WATERS

Various technologies have been used for the elimination of waste water discharged after reasonable cleaning and treatment into water courses. Such technologies are based on physical, physical-chemical, chemical or biological principles. Sorption ranks among the physical-chemical technologies. Within the sorption, sorbents are used to increase the concentration of a fluid medium component in a phase boundary where the fluid medium component borders on condensed media.

3.1 Sorbents

Absorption, adsorption and chemical sorption features of the sorbents make it possible to immobilise heavy metal cations. Efficient sorbents are substances with heavily disrupted porous surfaces. An adsorption activity of the surface is closely related to a flexure radius of local surface irregularities. The adsorption capacity is the highest in peaks and lower in edges. It decreases on poles, reaching the lowest values in hollows. A typical feature of good sorbents is a big specific surface being several hundreds $m^2.g^{-1}$. Certain natural materials or industrial wastes with a high sorption capacity can be used to absorb heavy metal cations. All this considerably reduces heavy metal disposal costs. Cheap sorbents include: lignin, chitin, seaweed/algae, zeolites, xanates, clay, fly ash, torf, sand with sand grains covered with iron oxide, or modified cotton or wool [5].

3.2 Materials

Three types of adsorbents have been used when experimenting in elimination of Cu from waste waters: bentonite , synthetic zeolite and slovakite that swell in the water.

Bentonite ranks among hydrated aluminosilicates, the key component being montmorrillonite.

Synthetic zeolite ranks among aluminosilicates. It was produced by zeolitisation of fly ash from power generation. The swelling level is 153.3 % by weight.

Slovakite is an inorganic composite sorbent produced from purely natural materials.

3.3 Experimental procedure

Bentonite - experimental measurements were carried out with pH = 6.0 at 25 ºC.

Synthetic zeolite -   the swelling level of the synthetic zeolite in water with pH = 5.0 at 25 ºC.

Slovakite - experimental measurements were carried out with pH = 5.0 at 25 ºC.

4 RESULTS AND DISCUSSION

The sorption of Cu, Zn and Pb ions has been measured experimentally for the initial concentration of 10 mg.l^{-1}. Sorption results of the elimination of copper ions from the waste water were satisfactory within approx. 60 s for all three sorbents: Slovakite, Bentonite and synthetic zeolite (zeolitised fly ash) (Fig. 1).

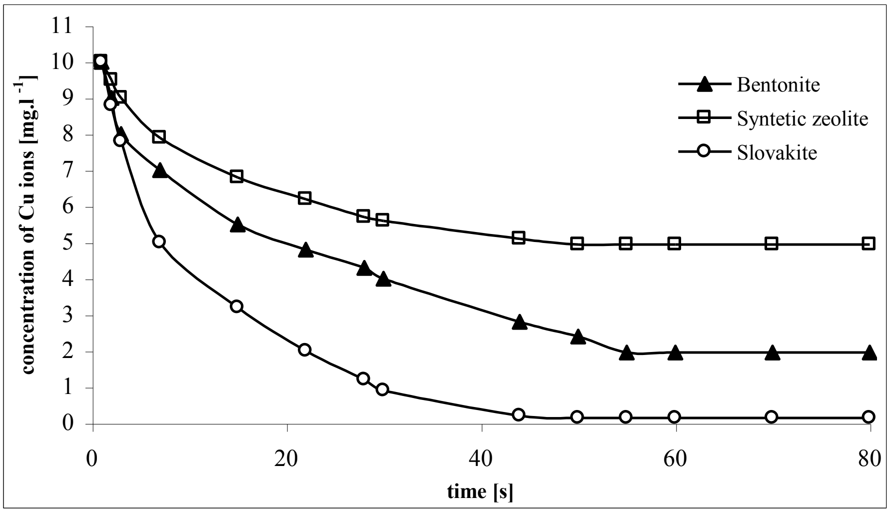

Fig. 1 Concentration-time relationship for the copper ion sorption

The Zn ions were absorbed within 80 seconds for all three sorbents during the experimental measurements (Fig. 2). If compared with the Cu ion sorption, about 20 seconds more were needed for the sorption.

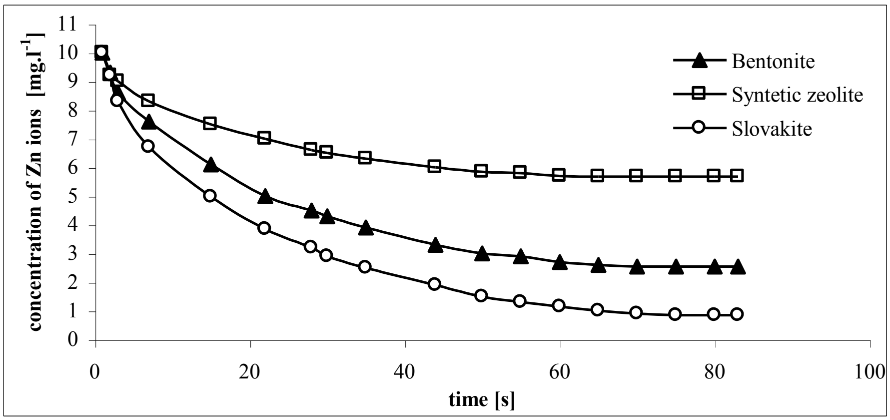

Fig. 2: Concentration -time relationship for the zinc ion sorption

The Pb ions were absorbed within 85 seconds for all three sorbents during the experimental measurements (Fig. 3). The sorption took most time, if compared with the sorptions of the Cu and Zn ions.

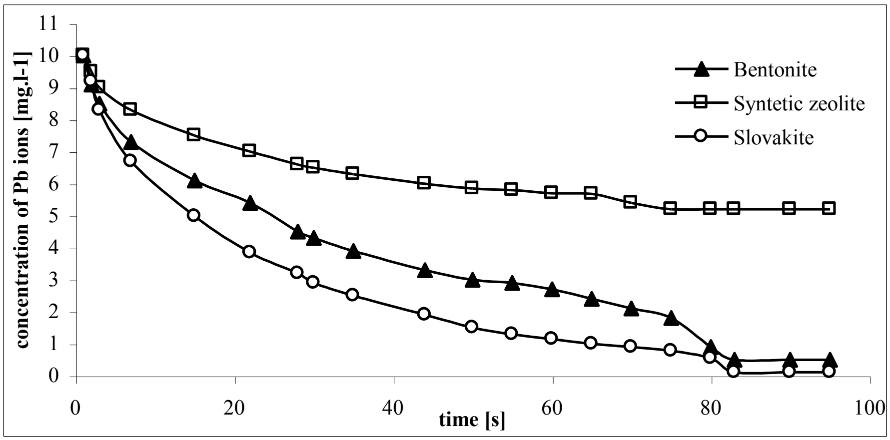

Fig. 3 Concentration -time relationship for the lead ion sorption

It clearly follows from graphical depictions of time aspects of the sorption of Cu, Zn and Pb ions that the synthetic zeolite has proved to be the best choice for the elimination of Cu, Zn and Pb, because it needs about 70 seconds to reach an equilibrium of the water solution saturation. Bentonite is the worst choice sorbent. According to experiments, it needed more than 80 s to absorb the Cu and Pb ions and approx. 80 s for the Zn ion absorption.

The sorption properties of the individual sorbents (see Fig. 4) with an experimental measurement of Cu, Zn and Pb ion elimination from waste water are relatively comparable. Major differences exist if the sorbents are confronted with each other. It follows clearly from the chart that describes efficiency of the Cu, Zn and Pb ion elimination from waste water that the best sorbents for separation of the Pb ions are bentonite and slovakite (since their sorption capacity exceeds 99%), and zeolite is the least suitable sorbent since the Pb ion elimination efficiency was below 41%. Results of Cu and Zn ion elimination were similar because the highest efficiency has been proved for the slovakite (91% and more than 98% for Zn and Cu, respectively). The synthetic zeolite proved to be the worst sorbent because the efficiencies of elimination of Zn and Cu ions were 44% and 51%.

The differences in the efficiencies of elimination of the heavy metal ions might be caused, among others, by the sorption properties of the sorbents being dependant on the volume of ion micro pores and, in particular, of a relative surface that varies considerably.

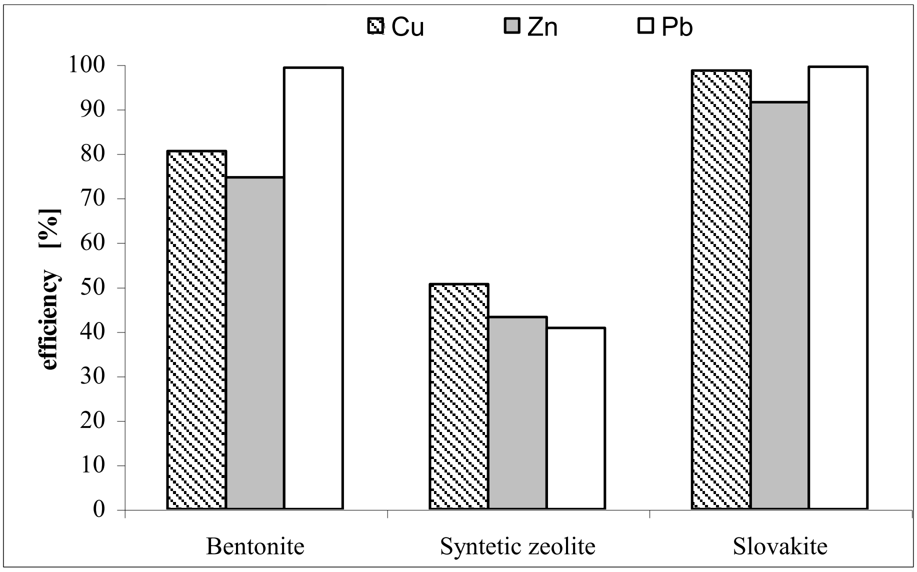

Fig. 4 Sorption efficiency for elimination of Cu, Zn and Pb ions by certain sorbents

5 CONCLUSION

The experiments above have proved clearly that the best sorbent for elimination of Cu, Zn and Pb ions from waste waters is slovakite. Its efficiency exceeded 91% for all those three heavy metals (98.6% for Cu, 91.5% for Zn and 99.48% for Pb).

Another sorbent under investigation was the bentonite. Its efficiency varied considerably (from 74.6% for the Zn ion to 99.31% for the Pb ions). Regarding the efficient elimination of the heavy metal ions under investigations, bentonite is recommended in particular for elimination of Pb from waste waters.

Synthetic zeolite has generally proved to be the least suitable sorbent because its elimination efficiency was below 51%.

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RESUMÉ

Antropogenní činností se do životního prostředí dostávají těžké kovy, které mohou představovat vážnou hrozbu pro živé organismy včetně člověka. Odstraňování těžkých kovů je neustále předmětem výzkumu, neboť používané technologie jsou hodně nákladné, případně málo účinné. Při technologiích odstraňování těžkých kovů se pozornost obrací na využívání různých přírodních, finančně málo náročných materiálů, nebo různých průmyslových odpadů.

Z těžkých kovů jsou předmětem tohoto výzkumu měď, zinek a olovo, které se často v odpadních vodách objevují.

Měď je biogenní prvek, který je nezbytný pro některé enzymatické reakce v organismech. Nadbytek mědi působí na živé organismy škodlivě a sloučeniny Cu působí toxicky na ryby. Olovo se z organismu obtížně vylučuje a ukládá se hlavně do kostí a může také způsobovat poruchy krvetvorby. Škodlivost zinku se projevuje hlavně na vodních organismech.

Pro odstraňování těžkých kovů z odpadních vod byly použity sorbety, u nichž se předpokládala dobrá adsorpční schopnost. Byl použit syntetický zeolit, který patří mezi alumosilikáty, dále bentonit, jehož hlavní složkou je minerál mont morillonit a slovakit, což je anorganický kompozitní sorbent připravený z přírodních surovin.

Sorbce iontů Cu, Zn a Pb byla ověřován na uvedených sorbetech. Výchozí koncentrace těchto kovů v roztoku byla 10 $mg.l^{-1}$. Byla sledována závislost koncentrace kovů na čase při sorbci a dosažená účinnost při použití jednotlivých sorbetů.

Z dosažených výsledků vyplývá, že nejsou velké rozdíly mezi adsorpcí iontů Cu, Zn a Pb. Značných rozdílů bylo dosaženo v účinnosti mezi jednotlivými sorbety.

Nejúčinnějším sorbetem se ukázal být slovakit, který u všech kovů vykázal účinnost nad 91 % a u olova až 99,48 %. Bentonit je vhodný pouze pro odstraňování Pb. Nejméně vhodný se ukázal syntetický zeolit, kdy účinnost odstraňování kovů z vody nepřesáhla 51 %.