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APPLICATION OF FIBROUS ION EXCHANGERS FOR REMOVAL OF HEAVY METALS FROM SEWAGE

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Abstract: The accumulation and removal of the heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) by fibrous ion exchangers at different stages of a typical biological wastewater treatment system, have been studied. In particular, the chelating ion exchanger FIBAN X-1 allows rapid and efficient sorption of the heavy metals from primary treated effluents. The degree of removal of Cu ion was about 17%; for both Cd and Pb the removal efficiency was >40%. Applied in batch process mode FIBAN X-1 should diminish the content of heavy metals in sewage and treated effluent.

Keywords: heavy metals, fibrous ion exchangers, municipal wastewater, sewage sludges.

INTRODUCTION

Heavy metals and their compounds, both organic and inorganic, are released to the environment as a result of anthropogenic activities (Sansalone, 2004). A significant amount of anthropogenic emission ends up in wastewaters (Karvelas et al., 2003). Heavy metals are naturally present in soil and water commonly in amounts that do not cause negative effects for living organisms. They do not undergo destruction or decomposition but they do show tendencies to accumulation and biomagnification in microorganism. Afterwards they may enter the human food chain (Ščančar et al., 2000).

Heavy metals are always present in municipal wastewaters, because they are commonly used in daily life. Their content in sewage depends on many local factors such as the kind of industry in the region, living standards of the society and the level of environmental awareness. Even domestic wastewater from households can contain significant amounts of heavy metals (Sörme and Lagerkvist, 2002).

Most sewage treatment plants treat wastewater by primary sedimentation followed by a biological process which uses activated sludge and secondary sedimentation. The primary treatment removes easily settleable solids and floating matter. The biological process, decomposes organic contaminants susceptible to biodegradation. The main purpose of biological systems is the removal of organic contaminants by microorganisms of the activated sludge. Removal of heavy metals is only a side effect of the processes (Arican et al., 2002). The known toxicity of heavy metals in the environment also influences the biological processes in wastewater treatment plants (Madoni et al., 1996). Moreover, the effectiveness of purification processes affects the amount of heavy metals discharged to the receivers (Chua, 1998).

There are two final products in a wastewater treatment plant: sewage sludge and treated effluent. Heavy metals that are present in municipal wastewater during the treatment processes are distributed between those two final products. The amount of heavy metals in sewage sludge or the amount that remains in treated effluent depends on many factors and it differs for different wastewater treatment plants (Kangala and Chipasa, 2003; Santarsiero et al., 1998). Heavy metals present in sewage sludge and in the treated effluent as well, may have a negative influence on the environment (Chua, 1998). Thus, in order to minimize health risks, it is necessary to develop simple methods to allow the control of heavy metals flow in sewage treatment plants.

During wastewater treatment large amounts of sewage sludge are produced. The sludge from the biological purification contains organic and biogenic substances, mainly nitrogen and phosphorus compounds. Organic substances, micro and macro elements would allow their use in agriculture and in soil recultivation (Ščančar et al., 2000). The use of sewage sludge as a source of nutrient substances and organic matter is possible when the concentration of heavy metals in sludge is below acceptable limits (Fytianos and Charantoni, 1998). Different chemical substances and sorbents to remove heavy metals from the sludge could be used (Prasad and Freitas, 2000; Soon-Oh Kim et al., 2002). Interesting attempts have been made to treat the sludge with sulfuric acid and subsequently to remove heavy metals by means of magnetic ion exchangers. The magnetic materials enable ready recovery of the loaded resin from the sludge in order to their regeneration (Bolto and Pawlowski, 1987).

Removal in the first step would allow reduction of the heavy metals content in municipal sewage. An application of ion exchange techniques for minimizing the load of heavy metals seems to be a very promising solution. Because of the very large volume of the effluent, conventional ion exchange techniques cannot be applied. However, synthesis and development of new ion exchange materials opens new possibilities. One possibility is the use of magnetic ion exchangers (Bolto and Pawlowski, 1987). Another possibility is to use fibrous ion exchangers. Textile materials made of polymers with chemically active functional groups have a unique combination of properties (Soldatov et al., 2003). On one hand, they fulfill the functions of ion exchangers while, on the other, they can function similarly to conventional textile materials such as cloth, non-woven fabrics, filters etc. This unique combination of the properties of textile ion exchange materials predetermines their advantages compared to granular ion exchangers in many processes (Soldatov et al., 1999). Along with conventional column processes, ion exchange textile materials can be applied in form of continuous moving bands, apparatuses combining the functions of mechanical and ion exchange filters. They also make possible the construction of principally new ion exchange contactors different to conventional apparatus and unsuitable for granular ion exchangers. High sorption rates by fibrous ion exchangers combined with high permeability of the filtering bed is their universal property.

Thus it seems likely that the properties of fibrous ion exchangers will allow efficient removal of heavy metals from sewage. The high efficiency of fibers with iminodiacetate groups in removing heavy metal ions from water has already been demonstrated (Soldatov et al., 1999).

MATERIALS AND METHODS

The fibrous ion exchangers FIBAN K-3, FIBAN K-4, FIBAN X-1 synthesized by the Institute of Physical Organic Chemistry of the Belarus National Academy of Sciences in Minsk (Belarus) were used in the current experiments. FIBAN K-3 is a product of hydrolysis of polyacrylonitrile fiber cross-linked with diethylenediamine. FIBAN K-4 is a product obtained by post-irradiation grafting of polyacrylic acid (PAA) into the polypropylene staple fiber. FIBAN X-1 is also an acrylic base fiber containing iminodiacetic and carboxylic functional groups (http://ifoch.bas-net.by/fiban_engl.htm by 2008.034.05).

Samples of sewage and treated effluent were collected from the Lublin Wastewater Treatment Plant.

Values of pH were measured by a combined glass electrode HI 1131B connected to a pH meter HANNA HI 932. The heavy metal concentrations were determined by atomic absorption spectrophotometer (HITACHI Z-2000). The standard solutions of heavy metals were supplied by Merck. All other chemicals were of analytical grade. The ultra pure water was obtained using a Millipore Milli-Q system.

Influence of pH on the heavy metals sorption

A portion of 50 mg of fibrous ion exchanger was added to 50 ml of the solution containing 2.5 ml of 2 M HCl and 0.5 ml of 0,01 M solution of a studied heavy metal. After mixing for 20 minutes the pH of the solution was measured and 0.25 ml sample was taken for the heavy metal analysis. Subsequently, a portion of 2 M KOH was added to the remaining solution. Such experiments were carried out with ion exchangers FIBAN K-3, FIBAN K-4 and FIBAN X-1 for each of the heavy metals (Cu, Cd, Ni, Pb, Cr, Zn) studied. Representative results obtained are presented in Figs. 1 – 2.

Sorption isotherm

The sorption isotherms were obtained in static conditions from the acetic buffer solution with pH = 6.00 and Na^+ concentration 0.19 mol/dm^3. A sample (50 mg) of the fibrous ion exchanger in H-form was added to 50 ml of the solution containing the studied heavy metal ion in the concentration range 0.00002 - 0.001 M. The equilibrated solutions were analyzed for the heavy metal content after 2 hours of mixing. The experimental isotherms were obtained for sorption of Cu, Cd, Ni, Pb, Cr, Zn onto the fibrous ion exchangers FIBAN K-3, FIBAN K-4 and FIBAN X-1. Typical results are shown in Figs. 3 – 4.

Influence of contact (mixing) time

A sample of 0.1 g of FIBAN X-1 in H-form was added to 1 dm^3 of the filtered sewage. After 1, 3, 5, 10, 15, 20, 25, 30, 45 and 60 minutes of mixing, 5 ml samples of the solution were collected for heavy metals content analysis. Some data characterizing the studied dependence are presented in Fig. 5.

Removal of heavy metals from sewage in static runs

In this series of tests each ion exchanger, in Na-form, was examined separately for its ability to remove heavy metals.

Typically, a sample of ion exchanger (0.1g) in Na-form was added to 1 dm^3 of the filtered sewage or primary treated effluent. 50 ml of the solution was taken for the heavy metals analysis after 1 hour of mixing. The fibrous ion exchanger was placed in a small plastic column, washed with deionized water and regenerated with 50 ml of 4% HNO_3 solution. The regenerant solution was analyzed for heavy metals content. Such experiments were carried out every two weeks for filtered sewage and primary treated effluent collected from Lublin WTP in the period from January to June of 2005. The average results are presented in Figs. 6 –7.

Removal of heavy metals from sewage in a column process

A sample of 1 g of the fibrous ion exchanger FIBAN X-1 in Na-form was placed in a plastic column of 1 cm diameter forming a filtering layer of 3 cm thick. 1 dm^3 of the filtered sewage or primary treated effluent was passed from the bottom to the top of the column (flow rate 6 m/h). The effluent was analyzed for the heavy metals content. The column was washed with deionized water and regenerated with 50 ml of 4% HNO_3 solution. The regenerant solution was analyzed for heavy metals content as well. The average obtained results in the period of 01-06.2005 are presented in Fig. 8.

RESULTS

The results of the tests described above are presented in Figs. 1-9. The influence of pH on the sorption of heavy metals (represented by Cu and Cd) from aqueous solutions onto fibrous ion exchangers is presented in Figs. 1-2.

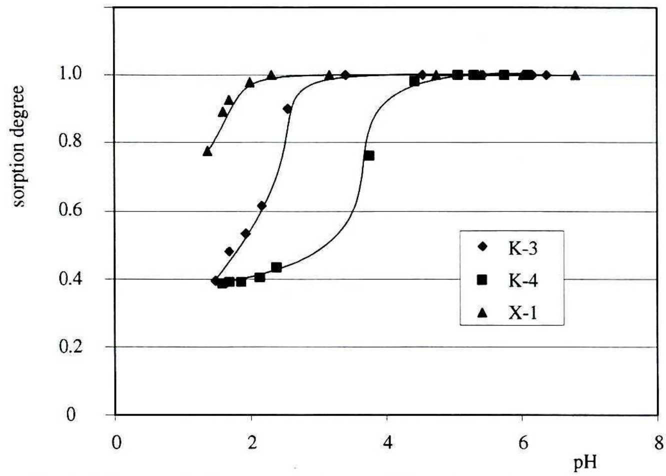

Fig. 1. Influence of pH on sorption degree of Cu on fibrous ion exchangers

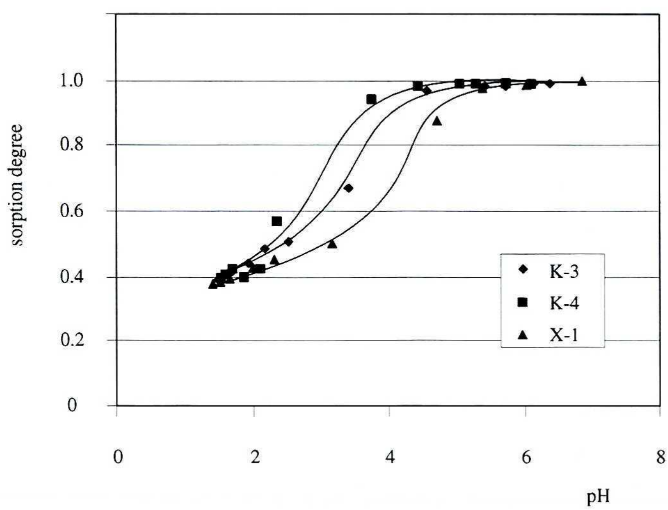

Fig. 2. Influence of pH on sorption degree of Cd on fibrous ion exchangers

Despite the fact that all three studied ion exchangers share a common dominant functional group (-COOH), their sorptive properties towards copper and cadmium ions are strikingly different. To understand this difference it is necessary to consider the structure of the ion exchangers and the acidity parameters of their functional groups. Fiber FIBAN K-4 is a product of radiochemical grafting of acrylic acid into polypropylene fiber. No other functional groups except -COOH (4.25 meq/g), are present in its structure. The average pK, their main acidity parameter, of these groups is 5.3. Ion exchanger FIBAN K-3 is a product of hydrolysis of polyacrylonitrile fiber cross-linked with diethylenediamine. It contains, in addition to 5.0 meq/g of carboxylic acid groups, 2.1 meq/g of secondary amine groups. The pK of the acidic groups is equal to 5.0. FIBAN X-1 is also an acrylic base fiber containing iminodiacetic groups 1.5 meq/g with a pK for the first ionization stage of the functional group equal to 3.2.

Comparing the pK values of the functional groups of the ion exchangers it becomes evident that the selectivity of sorption of Cu^{2+} and Cd^{2+} ions is not directly connected with their acidic strength. Probably, the sorption of the heavy metals takes place via the formation of complexes between the functional groups and the ions. In such complexes both the ionized and non-ionized carboxylic acid groups can act as ligands of the heavy metal ion. It is known that Cu^{2+} forms strong complexes with iminodiacetic groups as well as (weaker) complexes with amino and carboxylic acid groups. The Cd^{2+} cation complexes are weaker than those of Cu^{2+} with iminodiacetic and amino groups but stronger with carboxylic acid groups. The behavior of Ni^2+ is similar to that of Cu^{2+}, on the other hand, Pb^{2+} behaves somewhat similar to Cd^{2+}. Comparing the data in Fig. 1 with these a good correlation between the pH values at which the Cu^{2+} sorption reaches 80% of the total amount of the ion in the solution (1.8, 2.5 and 3.5 for FIBANs X-1, K-3 and K-4) respectively, is immediately evident. Another selectivity series is observed for Cd^{2+}: ion èxchanger FIBAN X-1starts absorbing this ion at the highest pH values. In accordance with the pK values of the functional groups the pH of 80% sorption are the lowest for FIBAN X-1 reflecting the fact that ionization of the carboxylic ligands favors formation of stronger ion-polyelectrolyte complexes. Nevertheless, it is obvious that the complex formation starts at pH values significantly below those at which massive ionization of the functional groups may occur. At pH values as low as 2 the degree of sorption reaches at least 40%. This can only be due to formation of the complexes with non-ionized carboxylic acid groups. This conclusion relates only to very low degrees of loading of the ion exchangers with the heavy metal ions, which are as low as fractions of the percent of the total capacity of these fibers according to these ions and achievable at higher pH values. Probably the ion exchangers contain some amounts of especially suitable sorption centers for the complex forming ions functioning as their efficient traps.

In conditions under which the –COOH groups is largely dissociated (pH=6.00, $[Na^+]$=0.19 M) the principle regularities of the heavy metal ions remain the same as described above, while some differences in detail may occur. They are seen from the sorption isotherms in Figs. 3 and 4 illustrated with Ni^{2+} and Pb^{2+} sorption. For the Ni^{2+} ion the most selective ion exchangers appeared to be FIBAN X-1 and FIBAN K-3. Both of them have nitrogen-containing groups able to form an additional coordinating bond with Ni and Cu cations. In contrast the Pb cation is most selectively absorbed by the monofunctional carboxylic acid cation exchanger. The nitrogen atom of the iminodiacetic groups may play a double role. On one hand it favors ionization of the carboxylic acid groups shifting the complex formation to the higher acidity of the solution. For the same reason it weakens the covalent constituent of the bond forming between the cation and the oxygen atom of the carboxylic acid group. On the other hand, it can play a role as an additional ligand in the complex. This explains why Pb and Cd cation are more strongly absorbed by carboxylic acid ion exchange and Cu, Ni and Co cations – by the ion exchangers with iminodiacetic groups.

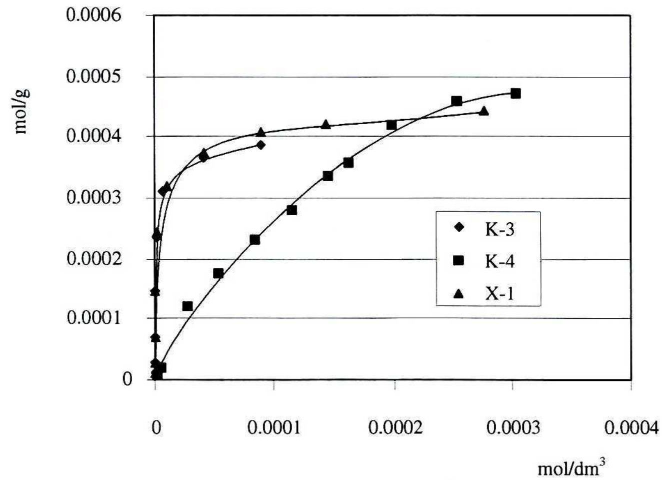

Fig. 3. Experimental sorption isotherms of Ni on fibrous ion exchangers

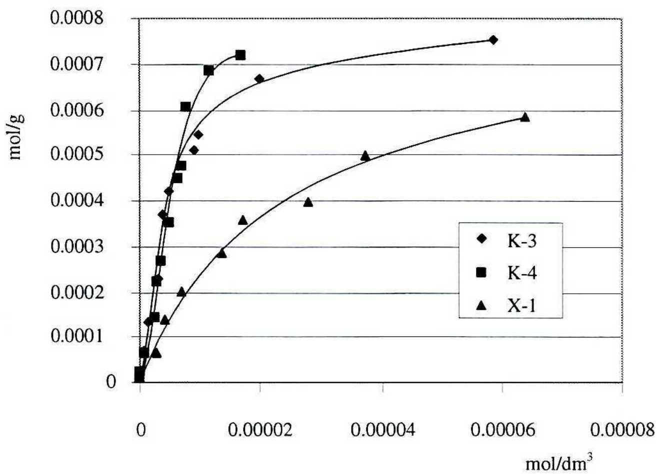

Fig. 4. Experimental sorption isotherms of Pb on fibrous ion exchangers

Influence of contact (mixing) time

The influence of contact time of fibrous ion exchanger with wastewater on the degree of sorption of the heavy metals is illustrated by Fig. 5.

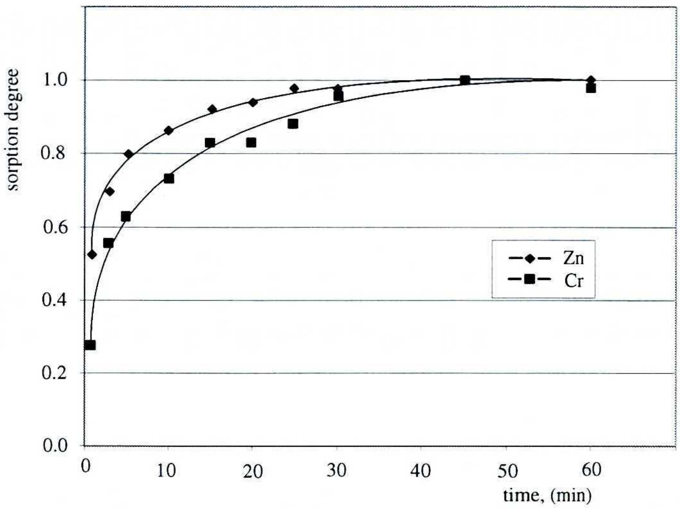

Fig. 5. Influence of contact time of fibrous ion exchanger Fiban X-1 with sewage on sorption of heavy metals (static conditions, dose of ion exchanger 0.1 g/dm^3)

As examples, the sorption of Zn and Cr onto FIBAN X-1 were chosen. This ion exchanger was discussed above as the most suitable for heavy metals removal while its selectivity towards Zn and especially Cr is rather low. It is evident that the degree of sorption of heavy metals increases with increased contact time. To obtain sorption at the level of 50% of the maximum sorption in the case of Cr, a contact time of nearly 3 minutes is needed, while for Zn 1 minute suffices. In practice, sorption of heavy metals from filtered sewage by fibrous ion exchanger FIBAN X-1 is complete when the contact time is 30-45 minutes depending on the removed heavy metal.

Removal of heavy metals from sewage by means of fibrous ion exchangers

The efficiency of heavy metal removal from filtered sewage and from primary treated effluent for single laboratory experiments are presented in tables 1 – 3. The average removal degrees of heavy metals from sewage calculated for twelve research series repeated twice monthly in the period of 02-07.2005 are illustrated in Figs 6 – 8.

Table 1. Concentrations of heavy metals in filtered sewage treated in static conditions with fibrous ion exchangers Fiban X-1 and Fiban K-4

Sample	Concentration (ppb)					
	Cd	Cr	Cu	Pb	Ni	Zn
Filtered sewage	5.8	12.6	20.9	4.6	12.3	163.0
Treated with Fiban X-1	4.5	10.9	19.2	3.2	7.1	94.6
Treated with Fiban K-4	5.4	11.1	16.4	3.3	10.5	129.1

Table 2. Concentrations of heavy metals in primary treated effluent purified in static runs by means of fibrous ion exchangers Fiban X-1 and Fiban K-4

Sample	Concentration (ppb)					
	Cd	Cr	Cu	Pb	Ni	Zn
Primary treated effluent	5.4	17.9	38.5	8.8	19.8	641.2
Treated with Fiban X-1	3.1	13.1	32.0	4.9	14.6	411.9
Treated with Fiban K-4	4.5	13.3	31.9	6.2	14.9	501.3

Table 3. Concentrations of heavy metals in filtered sewage and primary treated effluent purified in dynamic conditions by means of fibrous ion exchanger Fiban X-1

Sample	Concentration (ppb)					
	Cd	Cr	Cu	Pb	Ni	Zn
Filtered sewage:						
- initial	2.7	4.9	25.3	5.1	18.0	134.5
- purified with Fiban X-1	1.9	4.1	22.3	3.5	9.9	79.8
Primary treated effluent:						
- initial	4.6	11.3	40.1	7.3	21.2	486.1
- purified with Fiban X-1	2.9	7.4	33.9	3.9	13.8	287.6

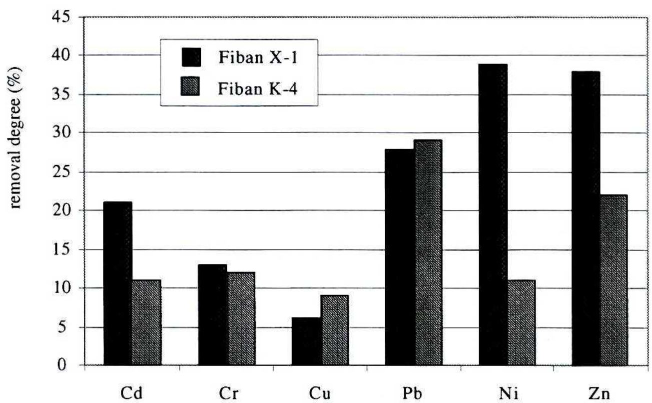

Fig. 6. Average degree of removal of heavy metals from filtered sewage using fibrous ion exchangers Fiban X-1 and Fiban K-4 in static runs

From the results it is seen that, under static conditions, higher efficiencies of heavy metal removal were generally obtained for FIBAN X-1 for filtered sewage and primary treated effluent. There were only two exceptions to this generalization, both noted for filtered sewage, where FIBAN K-4 was slightly more efficient in removing of Cu and Pb, compared to the results obtained for Fiban X-1. In the case of Cr removal from wastewater both ion exchangers provided similar results. Furthermore, it was observed that using fibrous ion exchanger FIBAN K-4 for removing Zn, Cd and especially Ni is less effective than applying Fiban X-1. A clearer situation is observed for the primary treated effluent where application of FIBAN X-1 for heavy metals removal yielded better results compared to those obtained with FIBAN K-4 (Fig. 7). The results show that FIBAN X-1 used in static conditions with primary treated effluent caused the removal of ca. 41% of Cd, 25% of Cr, 17% of Cu, 44% of Pb, 27% of Ni and 33% of Zn.

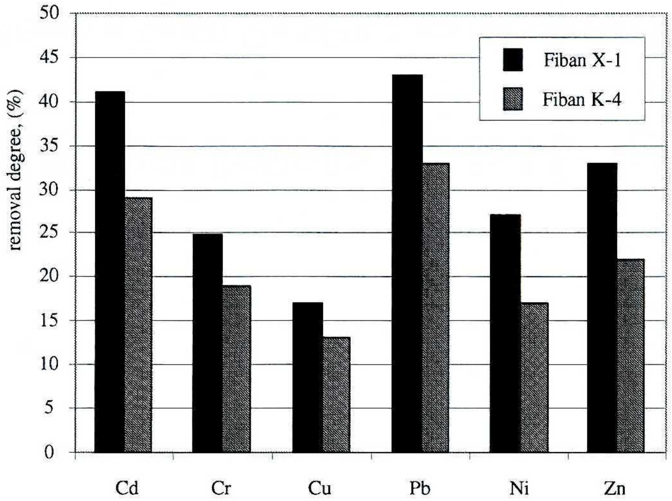

Fig. 7. Average degree of removal of heavy metals from primary treated effluent using fibrous ion exchangers Fiban X-1 and Fiban K-4 in static runs

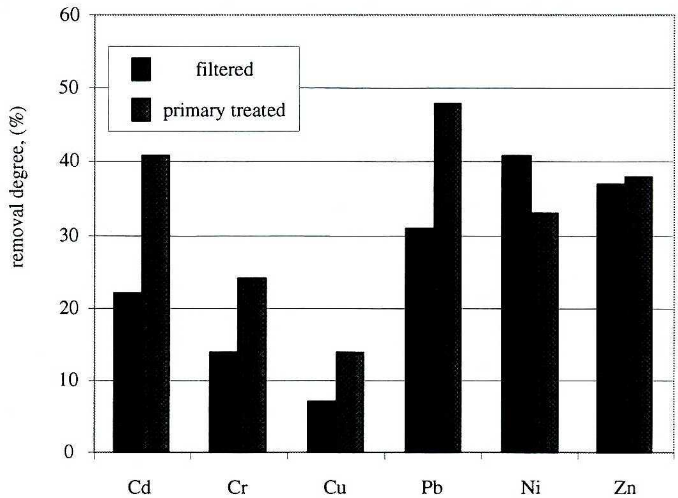

Fig. 8. Average degree of removal of heavy metals from primary treated and filtered sewage using fibrous ion exchanger Fiban X-1 in column process

Applied in dynamic conditions FIBAN X-1 provided a higher efficiency of heavy metal removal, especially in the case of primary treated effluent (see Fig. 8). Its use in column processing reduces the contents of Cd, Cr, Cu, Pb, Ni, Zn in primary treated sewage to about 40%, 25%, 15%, 50%, 32% and 38% of the original, respectively.

The results obtained confirm that fibrous ion exchangers could be used for control of the flow of heavy metals in a municipal sewage treatment plant. Fibrous ion exchangers, due to their unique structure, may be easily applied for removal of heavy metals:

- from sewage during primary treatment,
- from primary treated effluents,
- from secondary treated effluent.

The potential possibilities for that are presented in Fig. 9.

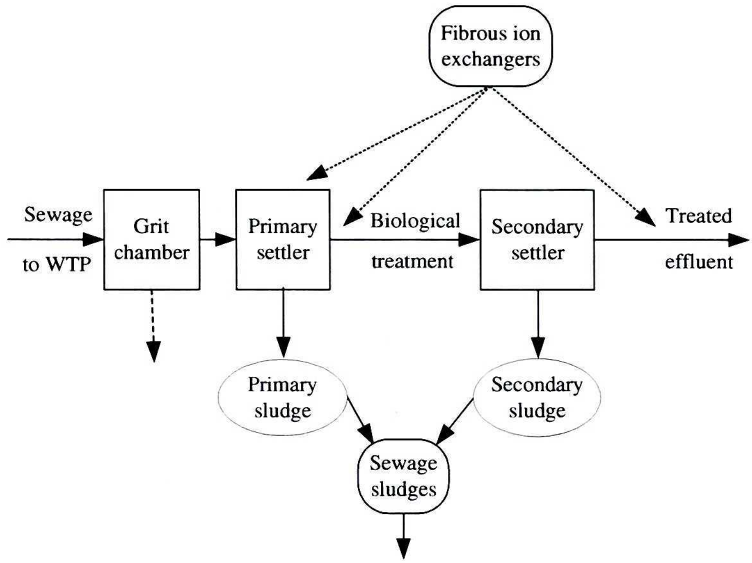

Fig. 9. Possible applications of fibrous ion exchangers to control the flow of heavy metals

CONCLUSIONS

From the results of laboratory studies on the application of fibrous ion exchangers for control of the flow of heavy metals during the sewage treatment process, we conclude the following:

The efficiency of heavy metal removal by means of fibrous ion exchangers is strongly pH-dependant. The carboxylic acid fibrous ion exchanger FIBAN X-1, having chelating functional groups, effectively sorbs some heavy metals at pH values around 2. For all fibrous ion exchangers at pH values ≥ 4, efficient sorption of all the heavy metals studied was found.

Under static conditions a higher efficiency of heavy metal removal was observed for the chelating fibrous ion exchanger FIBAN X-1 which reduced the contents of Cd, Cr, Cu, Pb, Ni, Zn in primary treated sewage by about 41%, 25%, 17%, 44%, 27% and 33%, respectively. Application of FIBAN X-1 in a column process assured the following removal efficiencies of heavy metals from primary treated sewage: 15% of Cu, 25% of Cr, 35% of Ni and Zn, 40% of Cd and nearly 50% of Pb. Thus, it appears that fibrous ion exchangers, due to their unique structure, might be used for control and removal of heavy metals at several stages in typical municipal biological sewage treatment plants.

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