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## **EFFECTIVENESS OF CHROMIUM COMPOUNDS(VI) REMOVAL FROM WATER ON DIATOMITE BEDS**

### **EFEKTYWNOŚĆ USUWANIA ZWIĄZKÓW CHROMU (VI) Z WODY NA ZŁOŻACH DIATOMITOWYCH**

*W artykule przedstawiono badania laboratoryjne, których celem było określenie efektów usuwania związków chromu (VI) z wody w procesie sorpcji i koagulacji przy użyciu diatomitów karpackich. Przeprowadzono je w warunkach dynamicznych metodą filtracji, na złożu diatomitowym o granulacji 0,75 - 1,2 mm, z optymalną prędkością filtracji 4 m/h, dla stężenia chromu w uzdatnianej wodzie  $C_o = 1 \text{ mg/dm}^3$ . Skuteczność sorpcji związków chromu w wyniku filtracji na złożach diatomitowych była niewielka (uzyskana redukcja  $\text{Cr}^{+6}$  wyniosła zaledwie 25%). Dużo bardziej efektywne okazało przeprowadzenie koagulacji kontaktowej z zastosowaniem reagentów: koagulantu  $\text{FeCl}_3$  oraz diatomitu pylistego jako środka wspomagającego sorpcję chromu. Najlepsze rezultaty uzyskano dla dawki koagulantu  $50 \text{ mg FeCl}_3/\text{dm}^3$ , diatomitu pylistego w ilości  $0,5 \text{ g/dm}^3$  oraz korekcie odczynu pH do 9,0. Uzyskane stężenie końcowe chromu w uzdatnianej wodzie wyniosło  $0,282 \text{ mg/dm}^3$ , co stanowiło 72 % redukcję chromu.*

## **1. Introduction**

Accelerating degradation of natural environment in Poland became a direct cause of reduction of drinking water resources as well as dramatic worsening of their quality. Chromium compounds belong to impurities which contribute to reducing of drinking water quality. Compounds of Cr(VI), which appear in water, constitute a very serious technological and engineering problem, which frequently requires radical changes in the entire water conditioning process and/or system, in order to achieve their removal [2].

Industrial wastewaters are the basic source of chromium compounds in water environment. Chromium release to natural environment takes place mainly in consequence of direct discharge of untreated wastewaters, incorrect production processes and incorrect storage of chromium-containing impurities/wastes. Major loads of chromium com-

pounds are discharged from metal plating (galvanizing) plants, plants producing paints and lacquers and tanneries [2, 12].

Compared to chromium (III), chromium (VI) is considered to be more bio-available because of its higher solubility, strong oxidizing properties and permeability through cell membranes. Besides, chromium (VI) compounds have toxic, mutagenic and carcinogenic effects on specific organisms [4, 6].

Observations show that more and more frequently their maximum concentrations are exceeded several times, and therefore it became particularly important to look for effective and economical methods of their removal. Processes of coagulation and sorption proved to be more effective than others, and they are implemented more and more often [1, 9, 13]. In sorption process, the applied sorbent is the most important element [7, 8]. It should be inexpensive, easily available and ecological. Diatomite materials may be counted among such sorbents [3, 10].

This paper concentrates on determining the effectiveness of chromium removal when using diatomite beds.

## 2. Methods of Study

The study was conducted on aqueous model solution. It was prepared on the base of tap water of pH 7.0 – 7.2, to which ( $\text{Cr}^{6+}$ ) chromium compounds were added form of potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ . The initial concentration of chromium in water was  $C_0 = 1 \text{ mg/dm}^3$ .

For testing, we used granular diatomite of granulation within 0.75-1.2 mm, dried at  $105^\circ\text{C}$ , from opencast mining field in Jawornik Ruski, located in northern part of Leszczawka deposit (Podkarpackie province) [5].

Refer to physicochemical properties of diatomite, presented w Table 1.

Tab. 1. Physical and chemical properties of diatomite

Parameter	Contents	Parameter	Contents
SiO <sub>3</sub>	68-73 %	Specific density	2,10-2,25 g/cm <sup>3</sup>
Al <sub>2</sub> O <sub>3</sub>	9-12 %	Bulk density of products depending of graining	0,4-0,9 t/m <sup>3</sup>
Fe <sub>2</sub> O <sub>3</sub>	4-6 %	Compression strength	25-60 MPa
Porosity	25-35 %	Thermal conductivity	0,25-0,30 kcal/m•h•°C
Absorbability	20-30 %	Roasting losses (900°C)	7-10 %

Tests were conducted on laboratory filter of diameter 0.035 m, filled with diatomite bed up to the height of 0.7 m, with gravitational (*downward*) flow. Diatomite mass of the filter was 0.4 kg.

Sorption capacity at the bed breakthrough point (*rise of chromium concentration in the effluent*) was determined from the relationship:

$$P = V \bullet (C_0 - C_k) / M \quad (1)$$

where:

P – bed sorption capacity (mg/kg)

V – volume of conditioned water (dm<sup>3</sup>)

C<sub>0</sub>, C<sub>k</sub> – initial and final concentrations of chromium compounds (mg/dm<sup>3</sup>),

M – bed mass (kg)

Fresh diatomite bed was used for each series of tests. The study consisted of three parts:

- 1<sup>st</sup> part – determining the optimum rate of filtration,
- 2<sup>nd</sup> part – filtration of tested water through diatomite bed,
- 3<sup>rd</sup> part – surface coagulation on diatomite bed with the following reagents: sorbent of powdery diatomite and coagulant of ferric chloride (FeCl<sub>3</sub>).

The third part consisted of the following test series:

Defining optimum dose of powdery diatomite and coagulant,

Surface coagulation with optimum dose of coagulant, FeCl<sub>3</sub>,

Surface coagulation with optimum dose of coagulant, FeCl<sub>3</sub>, and pH correction to 9.0 pH,

Surface coagulation with coagulant, FeCl<sub>3</sub>, and powdery diatomite,

Surface coagulation with coagulant, FeCl<sub>3</sub>, powdery diatomite and pH correction to 9.0 pH.

After each filtering of 5 liters of water a check determination of chromium compounds (Cr<sup>6+</sup>) in conditioned water was carried out.

### 3. Discussion of Results

Initial study (**part I**) had the objective to determine optimum rate of filtration. Tested water was passed through diatomite bed at following rates: 2, 4, 6, 8 m/h . After each filtering of 10 liters of water the conditioned water was analyzed. Refer to Table 2 for the selection of optimum rates of filtration.

Tab. 2. Choice of the optimum filtration speed

Speed of filtration [m/h]	Concentration of chromium in effluent [mgCr/dm <sup>3</sup> ]
8	0,941
6	0,834
4	0,720
2	0,696

The filtration rate of 4 m/h was adopted as optimum for further tests. The rate reduction to 2 m/h had only slight positive effect on the effectiveness of chromium removal. The determined retention time for  $v = 4$  m/h was 0.086 h (5.2 min).

During filtration of conditioned water through diatomite bed in the **second part of the study**, the mean concentration of chromium compounds in filtrate was  $C_k = 0,74 \text{ mg/dm}^3$ .

A clear growth of chromium concentration (to  $0.83 \text{ mg/dm}^3$ ), assumed as the bed breakthrough point, occurred after filtering  $95 \text{ dm}^3$  of water. The effectiveness of sorption of chromium compounds in filtration on diatomite beds was low (the  $\text{Cr}^{6+}$  reduction by merely 25 %). The bed sorption capacity, calculated from the formula (1), was  $P_1 = 60 \text{ mg/kg}$ .

In order to raise the effectiveness of removing of chromium compounds, the **3<sup>rd</sup> part of the study** was carried out while introducing in the process the following filtration reagents: coagulant,  $\text{FeCl}_3$ , and powdery diatomite as sorbent.

Refer to Table 3 for the results of selecting optimum powdery diatomite.

Tab. 3. Choice of the best of the powder diatomite dose

Dose of powder diatomite [g/dm <sup>3</sup> ]	Concentration of chromium in effluent [mgCr/dm <sup>3</sup> ]
0,1	0,816
0,5	0,593
1,0	0,520
2,0	0,515
5,0	0,478

When analyzing the obtained results, it may be noticed that differences in chromium concentration within diatomite dose range of 0.5 – 5.0 are small. Moreover, during filtration with doses of 2 and  $5 \text{ g/dm}^3$  in was noticed that filtration rate dropped because of bed clogging. On the basis of obtained results, the optimum dose of powdery diatomite,  $0.5 \text{ g/dm}^3$ , enabling approx. 41% reduction of chromium, was selected and applied in the subsequent part of the study.

The selection of the most favorable dose of coagulant covered the following doses of  $\text{FeCl}_3$ : 20; 30; 50; 80;  $100 \text{ mg/dm}^3$ . The vessel method was applied. The time of rapid mixing was 0.5 minute, while the slow mixing time was 15 min.

Refer to test results in fig. 1.

On the basis of obtained results, the dose of  $50 \text{ mg/dm}^3$  of coagulant, enabling approx. 41% reduction of chromium, the dose of  $50 \text{ mg/dm}^3$  of coagulant, was selected as optimum and applied in the subsequent part of the study as it enabled obtaining chromium concentration of  $0.63 \text{ mg/dm}^3$ , i.e. the reduction of chromium compounds in conditioned water by 37 %.

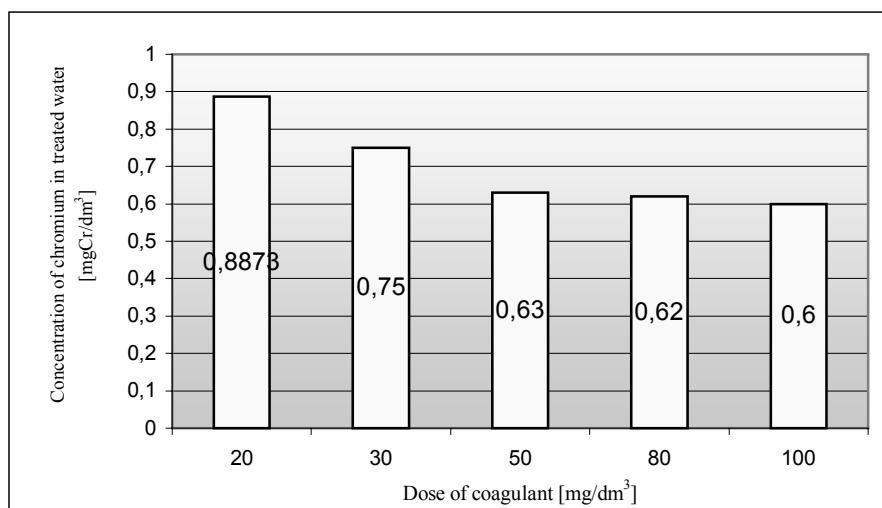


Fig. 1. Choice of the optimum coagulation dose

The results from consecutive series of studies (2–5), realized as coagulation, are presented in Table 4.

Tab. 4. Compilation of surface coagulation results after diatomite bed

No. of series, used reagents	Concentration of chromium in effluent [mgCr/dm³]	Reduce of chromium [%]
II coagulant dose FeCl <sub>3</sub> , 50 mg /dm³	0,39	61
III reaction correction to 9,0 pH, dose FeCl <sub>3</sub> 50 mg /dm³	0,36	64
IV diatomite dose 0,5 g/dm³, dose FeCl <sub>3</sub> 50 mg /dm³	0,31	69
V reaction correction to 9,0 pH, diatomite dose 0,5 g/dm³, dose FeCl <sub>3</sub> 50 mg /dm³	0,28	72

The 2<sup>nd</sup> series of filtration, with ferric chloride coagulant at the optimum dose, resulted in the reduction of chromium compounds by 61 %. Their concentration of in the effluent remained at  $C_k = 0.39 \text{ mg Cr}^{6+}/\text{dm}^3$  for approx. 32 hours, when 120 liters of water was filtered. The bed sorption capacity was calculated as  $P_2 = 183 \text{ mg/kg}$ .

In order to increase the effectiveness of coagulation with iron (III) salts, the water reaction was corrected to 9.0 pH in the subsequent series of studies. During the flow of 150 liters of tested water, the chromium concentration in the effluent oscillated at  $C_k = 0,36 \text{ mgCr}^{6+}/\text{dm}^3$ . Its dynamic growth happened after that time. For the bed breakthrough point assumed at that moment, the calculated sorption capacity was  $P_3=240 \text{ mg/kg}$ .

In order to reduce further the concentration of chromium in water, powdery diatomite was introduced in optimum dose ( $0,5 \text{ g/dm}^3$ ) to support surface coagulation in the subsequent series of study. The filtration lasted till the moment of bed colmating (flow rate drop to  $2.5 \text{ m/h}$ ). Water amount of 160 liters was passed, and the chromium concentration in the effluent remained at the level of  $0.31 \text{ mgCr}^{6+}/\text{dm}^3$  all through the filtration period. The bed sorption capacity was  $P_4=276 \text{ mg Cr}^{6+}/\text{kg}$ .

As the water pH raising to 9 contributed to reduction of chromium in the effluent and it extended the filtration cycle, the final series of filtration was carried out with water pH correction with the basic coagulant and powdery diatomite. The bed sorption capacity achieved in this series of the study was  $P_5=290 \text{ mg Cr}^{6+}/\text{kg}$  and chromium concentration in the effluent till the bed breakthrough point (bed colmating) stayed at the level of  $0.28 \text{ mgCr}^{6+}/\text{dm}^3$ .

Comparison of bed sorption capacities obtained in all filtration cycles, was presented in Figure 2.

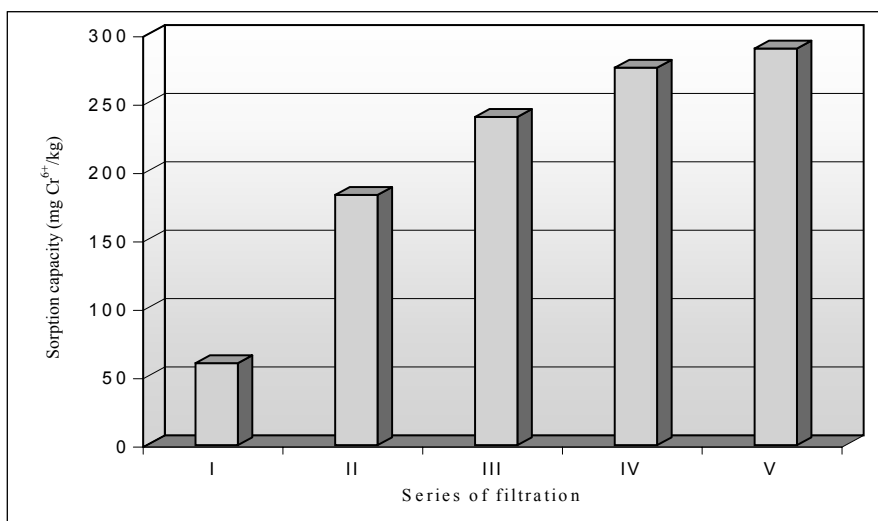


Fig. 2. Sorption capacity of filtration bad: I – filtration through diatomite bad, II – filtration through diatomite bad with coagulation  $\text{FeCl}_3$ , III – correction of reaction to 9 pH and filtration with coagulation  $\text{FeCl}_3$ , IV – filtration with coagulation –  $\text{FeCl}_3$  + powder diatomite, V – correction of reaction to 9 pH, filtration with reagents: coagulation  $\text{FeCl}_3$  + powder diatomite

The analysis of obtained bed sorption capacities indicates that the filtration through diatomite bed only was least effective. It lasted for the shortest time until the breakthrough point, the obtained chromium concentration in the effluent was the highest (reduction by just 25%) and therefore the lowest bed sorption capacity was obtained.

Application of surface coagulation, caused a significant rise in the effectiveness chromium compounds removal from conditioned water. The iron hydroxides, precipitated during hydrolysis, were effective in raising of bed sorption capacity, thus achieving lower chromium concentrations in the effluent during filtration, longer filtration time, and several times higher sorption capacities. In order to achieve the lowest solubility of the products of hydrolysis of the applied coagulant, the pH of the water was corrected to 9 during filtration in the 3<sup>rd</sup> and 4<sup>th</sup> series of the study. It also contributed significantly to raising the numbers of chromate ions removed from water. Introducing of powdery diatomite as the coagulation supporting agent in the 4<sup>th</sup> and 5<sup>th</sup> series of the study also contributed to growing effectiveness chromium compounds removal. As a byproduct from diatomite fractioning, the powdery diatomite exhibits sorptive properties in relation to chromate ions [11]. Moreover, it contributes to raising of specific surface of generated flocculants, their better sedimentation in the bed and thus to raising the bed sorption capacity. The drawback to the use of that sorbent in the process of surface coagulation, may well be the too rapid silting up of the filtration bed (it depends to a high degree on its dose as well as on bed porosity). Better results from all filtration cycles were achieved with the use of coagulant,  $\text{FeCl}_3$  at the dose of  $50 \text{ mg/dm}^3$ , diatomite –  $0.5 \text{ g/dm}^3$ , as well as with raised pH of conditioned water.

#### 4. Conclusions

- Removal of chromate ions in the process filtration on diatomite bed exhibited low effectiveness (the achieved reduction  $\text{Cr}^{6+}$  was merely 25%).
- Application of surface coagulation with the use of ferric chloride ( $\text{FeCl}_3$ ) as coagulant lead to reduction chromium concentration in the effluent by approx. 60%, extending the filtration cycle and considerable (4–time) raising of sorption capacity of diatomite bed.
- Introducing diatomite powder to filtration as the agent supporting the surface coagulation process, contributed to raising of the effectiveness chromate ion removal from water.
- The best results were obtained when using: coagulant dose of  $50 \text{ mg FeCl}_3/\text{dm}^3$ , powdery diatomite in a quantity  $0.5 \text{ g/dm}^3$ , as well as pH correction do 9.0. The final concentrations of chromium in conditioned water was  $C_k=0,28 \text{ mg/dm}^3$  (which is tantamount to 72% reduction of chromium), the bed sorption capacity reached the value of  $P_5=290 \text{ mg Cr}^{6+}/\text{kg}$ .

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