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# USE OF THE EGGSHELLS
# IN REMOVING HEAVY METALS FROM WASTE WATER -
# THE PROCESS KINETICS AND EFFICIENCY

## ZAGOSPODAROWANIE SKORUP JAJ DO USUWANIA METALI CIĘŻKICH
## ZE ŚCIEKÓW - KINETYKA I SKUTECZNOŚĆ PROCESU

**Abstract:** Studies of the efficiency of Ni, Cu and Cd cations removal from water solutions were carried out, with the use of clay limestone, hen eggshells from eggs for consumption and hen eggshells after hatching, which main element is calcium carbonate. Hen eggshells are a waste product, which can be used as a substitute of clay limestone in removing heavy metals from wet flue gas desulphurisation installation. Mixed solutions of Ni, Cu and Cd were used in the research, with the composition similar to the waste water from wet flue gas desulphurisation installation: Ni (0.009-0.053 mmol/dm$^3$), Cu (0.008-0.057 mmol/dm$^3$) and Cd (0.003-0.008 mmol/dm$^3$). The metals were determined by flame atomic absorption spectrophotometry (F-AAS). Kinetics of the process was analysed and equilibrium parameters were estimated, taking into consideration changes of the solutions pH during the process duration. It was demonstrated that the dominating mechanism of cations removal is their binding in hydroxides and carbonates. The studies demonstrated comparable characteristics of hen eggshells versus clay limestone, in the context of their application in removal of heavy metal cations from solutions.

**Keywords:** hen eggshells, clay limestone, heavy metals, industrial sewage treatment

## Introduction

Hen eggshells, due to their chemical composition and structure, are a valuable raw material, which can be the source of calcium carbonate (CaCO$_3$ is over 94 % of a shell mass), e.g. in paper industry as a filler and pigment for coating, in food industry as a hardener and food dye (E 170), in agriculture for fertiliser manufacturing, in metallurgy as a flux in ladle desulphurisation, in construction, chemical, cosmetics and pharmaceutical industries. The research has been carried out in recent years on the possibility to use eggshells as a catalyst in the processes of biodiesel production [1, 2], lactose isomerisation [3], dimethyl carbonate synthesis [4] and as a sorbent in water treatment processes [5, 6], immobilisation of heavy metals in soils [7, 8], CO$_2$ binding (removing) [9].

Studies on the use of eggshells in sewage treatment process have also been carried out [10-14]. The effectiveness of water solutions purification depends on a number of factors, among others pH, concentration, sorbent particles size, dose and contact period,

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competitive sorption of ions [15, 16]. In this context, studies have been carried out aiming at increasing the process intensity by eggshells modification: thermal, e.g. calcination [17, 18], chemical [19, 20] and mechanical, e.g. grinding [21, 22].

The attempt to lower the process costs by using the mass-scale produced waste as sorbents, which are not activated by any additional process, is an important aspect [23].

In the context of eggshells use, industrial applications are still very few, at the current research stage. Therefore it is recommended to search for alternative methods of their use. The proposed method is to use this by-product as a substitute of clay limestone in the process of heavy metals removal from waste water in wet flue gas desulphurisation installations. Waste water from wet flue gas desulphurisation installations contain large quantities of heavy metals (Cu, Zn, Cd, Pb, Ni, Cr, Hg), large concentration of chlorides, sulphates, nitrogen compounds, the presence of organic substances and mineral suspensions [24]. The treatment process involves using clay limestone, mainly to precipitate heavy metals in the form of hydroxides and carbonates, in slightly alkaline environment (pH 8-9).

The aim of the carried out studies was to compare the efficiency of removal of Ni, Cu and Cd from water solutions, with the use of clay limestone, hen eggshells and hen eggshells after hatching, in the context of the possibility to use these materials to remove heavy metals from waste water in wet flue gas desulphurisation installations. Hen eggshells after hatching have different mass proportions of organic and non-organic substances, compared to the shells from eggs for consumption. The studies were carried out by measurements of the process kinetics and comparison of the efficiency of the prepared waste water treatment.

The hypothesis was accepted, that metal cations removal from solutions with the use of eggshells, similarly as with clay limestone, undergoes in consequence of chemical reactions, which lead to generation of sparingly soluble hydroxides and carbonates, which can be physically adsorbed on the shells' surface and not in consequence of a heterophasic ions exchange and chemical adsorption, as suggested by some authors.

## Materials and methods

Clay limestone (WM), hen eggshells for consumption (SK) and hen eggshells after hatching (SW) have been used in the study.

### Characteristics of the analysed material

Chemical composition and heat and thermophysical characteristics of eggshells are similar to widely used clay limestone. The compared materials have similar crystalline structure, however carbonates in eggshells have larger crystals [25]. Table 1 presents data on chemical composition of WM (own research) and SK [26].

Chemical composition of shells (SK) changes during incubation and their thickness is reduced [27]. Shells (SW) after 21 days of incubation contain approximately 15 % less calcium and approximately 20 % less magnesium [28]. Shells after hatching have more membranes under shell, which have good sorption characteristics with regard to metal cations [22, 29].

The indicated differences in chemical composition may influence the mechanism and efficiency of metal cations removal from water solutions.

Comparison of clay limestone and hen eggshells

| Chemical compound | WM [%] | SK [%] |
|---|---|---|
| $CaCO_3$ | 97.20 | 94 |
| MgO | 0.61 | - |
| $Fe_2O_3$ | 0.38 | - |
| $Al_2O_3$ | 0.26 | - |
| $SiO_2$ | 0.87 | - |
| $Ca_3(PO_4)_2$ | - | 1 |
| $MgCO_3$ | - | 1 |
| Organic compounds | - | 4 |
| Other | 0.68 | - |

## The research methodology

WM samples sized < 90 µm, used in removal of heavy metals from waste water in wet flue gas desulphurisation installations, were used in the studies. Hen eggshells were obtained from a poultry hatchery. SK shells were obtained from unfertilised eggs and SW shells were a by-product after chicken hatching. Shells were rinsed in deionised water, keeping under shell membranes; next they were fragmented (to approximately 50 mm diameter) and dried to dry mass at 105 °C. Next they were ground in a knife mill and sieved out on a 100 µm mesh sieve. The fraction < 100 µm was used in the research.

The research was carried out with the use of 200 cm$^3$ solutions, in which 1 g of WM, SK or SW was placed. The process of metals removal, with intense stirring (500 rotations/min), was carried out for 3 hours at room temperature. The solution samples (approximately 1 cm$^3$), for determining the process kinetics parameters, were taken every 30 minutes. The initial solution pH was within the range 4.6-5.4. Metals in the solution were determined by flame atomic absorption spectrophotometry (F-AAS).

## Quality and quality assurance

The absorbing atomic spectroscope iCE 3000 made by *Thermo Electron* Corporation, USA, was used to determine heavy metals concentrations in the solutions. The pH of solutions were immersed was measured with a CP551 pH-meter from Elmetron Sp.j. from Zabrze (PL). The absolute error of readings was $\Delta$pH = 0.02. MERCK reagents were used to prepare the solutions.

Uncertainty of determination of the analysed metals by AAS method did not exceed 10 %. Limits of determination (*IQL*) for Ni, Cu and Cd were respectively [mg/dm$^3$]: 0.024, 0.015 and 0.010.

Detailed data for the equipment, together with an evaluation and quality assurance, were published in [30].

## Results interpretation method

The pseudo-second-order reaction model [31, 32] was applied to describe kinetics of metal cations removal, based on the relation:

$$\frac{t}{q_{M(t)}} = \frac{1}{k" \cdot \left( q_{M(eq)} \right)^2} + \frac{1}{q_{M(eq)}} \cdot t \qquad (1)$$

where: $k$" - constant speed of pseudo-second-order reaction, $q_{M(t)}$ - metal concentration in bound form after time $t$, $q_{M(eq)}$ - metal concentration in bound form in equilibrium.

Concentration of metals in bound form, related to the mass of 1 g of WN, SK or SW, was calculated on the basis of the results of initial and instantaneous concentrations measurements in the solution. Concentrations were expressed in mmol/g for comparison, in the kinetics description.

Concentrations of $M^{+2}$ metal cations, which were in equilibrium with $M(OH)_2$, were determined on the basis of the relation:

$$pH_{prec.} = z^{-1} \cdot (14 \cdot z - \log C_{M}{}^{+z}{}_{(eq)} - pK_{sp}) \tag{2}$$

where: $pH_{prec.}$ - the pH value, above which hydroxides precipitate, $z$ - cation valence, $C_{M}{}^{+z}{}_{(eq)}$ - copper cations concentration in the solution [mol dm$^{-3}$], $K_{sp}$ - solubility product constants ($pK_{sp} = -\log K_{sp}$), for nickel, copper and cadmium hydroxide, values of $pK_{sp}$ are, respectively: 15.3, 19.3 and 14.1.

The loss of metal cations (removal efficiency), $U$, from the solution was calculated on the basis of the relation:

$$U = \frac{C_0 - C_1}{C_0} \cdot 100 \,\% \tag{3}$$

where: $C_0$ and $C_1$ - initial and final concentrations of metal cations in the solution.

## Results and discussion

The studies of the Ni, Cu and Cd removal with the use of WM, SK and SW were carried out in the solutions with metal concentrations within the range determined in waste water in wet flue gas desulphurisation installations [24]. Table 2 presents the initial composition of the solutions.

Table 2

Initial composition of the solutions used in the research [mmol/dm$^3$]

| Metal | Solution I | Solution II | Solution III |
|-------|-----------|------------|-------------|
| Ni | 0.0090 | 0.0351 | 0.0532 |
| Cu | 0.0069 | 0.0381 | 0.0674 |
| Cd | 0.0033 | 0.0063 | 0.0078 |

Taking pH measurements before and after the process was an important parameter, indicating the process of precipitation of hydroxides of the studied metals (relation (2)). The results are presented in Table 3.

Table 3

Initial (0) and final (1) pH values of the solutions

| Solution | pH$_0$ | | | pH$_1$ | | |
|----------|--------|------|------|--------|------|------|
|          | WM | SK | SW | WM | SK | SW |
| I | 4.77 | 4.77 | 4.78 | 8.90 | 8.82 | 8.81 |
| II | 4.60 | 4.59 | 4.59 | 8.33 | 8.52 | 8.38 |
| III | 5.47 | 5.46 | 5.47 | 7.87 | 8.07 | 8.09 |

## Kinetics of the removal processes

The objective of assessment of heavy metals removal process kinetics parameters was to point out similarities and differences of the process, using WM, SK and SW. Figure 1 presents two different examples, indicating the influence of heavy metals concentration in a solution on the kinetics of the Ni and Cd removal process.
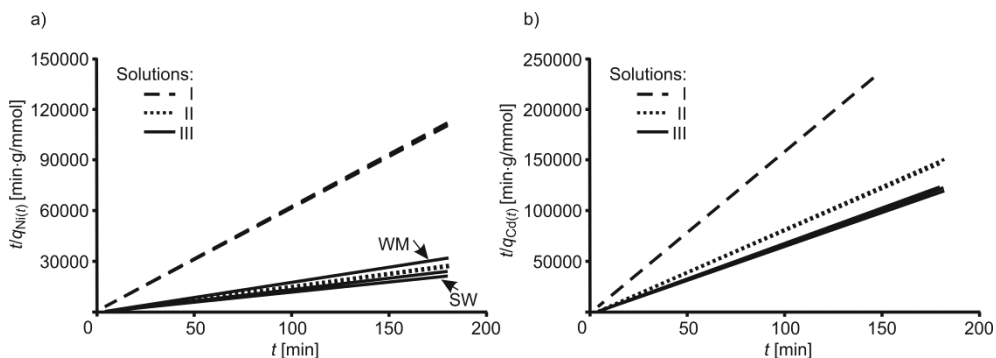


Fig. 1.  Kinetics of a) Ni and b) Cd removal from I-III solutions with the use of WM, SK and SW

The results presented in the graph in Figure 1a indicate similarities of the removal parameters, in the range of higher initial concentrations of nickel cations, and slightly better parameters with the use of SW versus WM, with the highest initial concentrations (Solution III). In relation to cadmium (Fig. 1b), similarly as in the case of copper, no differences in removal kinetics with WM, SK and SW were recorded (directional coefficients of the straight lines determined on the basis of relation 1 do not depend on the source of $CaCO_3$ origin, but only on the initial concentration of metals in the solution).

Table 4 presents data related to the values $q_{M(eq)}$ [mmol/g], determined on the basis of relation (1), indicating the concentration of metals in bound form in equilibrium, calculated values of metal cations concentrations in solution $c_{M(eq)}$ [mmol/dm$^3$], in equilibrium and, determined on the basis of relation (2), theoretical values of metal cations concentration values in solution $C_{M(eq)}$ [mmol/dm$^3$], being in equilibrium with hydroxide suspension. In this case, equilibrium referred to the recorded average final pH of the solution (Table 3). The values $q_{M(eq)}$ and $c_{M(eq)}$ presented in the table refer to the average values for WM, SK and SW and are different for initial concentrations of metals in the solutions I-III (Table 2).

Table 4

Values $q_{M(eq)}$, $c_{M(eq)}$ calculated on the basis of relation (1) and theoretical values of metal cations concentrations in a solution in equilibrium $C_{M(eq)}$ determined on the basis of relation (2)

| Solution | Ni | | | Cu | | | Cd | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_{M(eq)}$ [mmol/ g] | $c_{M(eq)}$ [mmol/ dm$^3$] | $C_{M(eq)}$ [mmol/ dm$^3$] | $q_{M(eq)}$ [mmol/ g] | $c_{M(eq)}$ [mmol/ dm$^3$] | $C_{M(eq)}$ [mmol/ dm$^3$] | $q_{M(eq)}$ [mmol/ g] | $c_{M(eq)}$ [mmol/ dm$^3$] | $C_{M(eq)}$ [mmol/ dm$^3$] |
| I | $1.7 \cdot 10^{-3}$ | $1.5 \cdot 10^{-3}$ | $1.0 \cdot 10^{-2}$ | $1.4 \cdot 10^{-3}$ | $9.4 \cdot 10^{-6}$ | $1.1 \cdot 10^{-6}$ | $6.0 \cdot 10^{-4}$ | $1.2 \cdot 10^{-4}$ | $1.7 \cdot 10^{-1}$ |
| II | $2.6 \cdot 10^{-3}$ | $6.5 \cdot 10^{-3}$ | $1.7 \cdot 10^{-2}$ | $7.6 \cdot 10^{-3}$ | $5.7 \cdot 10^{-6}$ | $7.6 \cdot 10^{-6}$ | $1.1 \cdot 10^{-3}$ | $9.4 \cdot 10^{-4}$ | $1.2 \cdot 10^{0}$ |
| III | $6.6 \cdot 10^{-3}$ | $2.0 \cdot 10^{-2}$ | $4.8 \cdot 10^{-1}$ | $1.4 \cdot 10^{-2}$ | $4.6 \cdot 10^{-5}$ | $4.8 \cdot 10^{-5}$ | $1.3 \cdot 10^{-3}$ | $1.2 \cdot 10^{-3}$ | $7.6 \cdot 10^{0}$ |

The results presented in the table are estimates. The values of concentrations $c_{M(eq)}$, determined from the pseudo-second-order equation (relation (1)) and the values $C_{M(eq)}$, determined from the relation (2) are of considerable importance. Similar values $c_{M(eq)}$ and $C_{M(eq)}$ with regard to copper may indicate that the final pH of the solution has the main influence on equilibrium. Increased pH value is a result of calcium carbonate dissociation: $CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}$, next, in hydrolysis: $CO_3^{2-} + H_2O \leftrightarrows HCO_3^- + OH^-$. In consequence, the equilibrium is achieved: $Cu^{2+} + 2OH^- \leftrightarrows Cu(OH)_2$. Much lower values of $c_{M(eq)}$ in comparison to $C_{M(eq)}$, in particular for Cd, may indicate a considerable influence on generation of insoluble carbonates during the process of removal of these metals cations from solutions. The values $K_{sp}$ for $NiCO_3$ and $Ni(OH)_2$ are on the level $10^{-7}$ and $10^{-16}$, for $CuCO_3$ and $Cu(OH)_2$ are on the level $10^{-10}$ and $10^{-20}$, and for $CdCO_3$ and $Cd(OH)_2$ are on the level $10^{-12}$ and $10^{-15}$. These values indicate relatively high, in comparison to the quoted examples, solubility of nickel carbonate and relatively small differences of the values $K_{sp}$ for $CdCO_3$ and $Cd(OH)_2$. The difference of $K_{sp}$ values may explain the results of previously discussed studies, presented in [33]. The initial, mol concentration of metal cations is also of importance.

These comparisons confirm and supplement the result of below presented studies on effectiveness of the studied metal cations removal from solutions.

## Effectiveness of metals removal

Figure 2-4 presents a comparison of effectiveness of $U$ removal (relation (3)) of the studied heavy metals from solutions with the use of clay limestone (WM), hen eggshells for consumption (SK) and eggshells after hatching (SW).
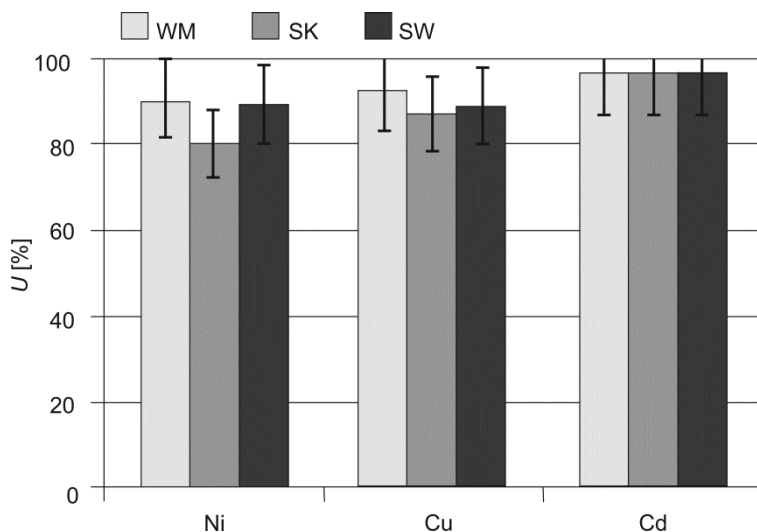


Fig. 2. Effectiveness of nickel, copper and cadmium cations removal from Solution I (Table 2) with the use of WM, SK and SW

The concentrations of Ni, Cu and Cd in Solution I did not exceed 0.01 mmol/dm³. In this range of concentrations, WM demonstrated the highest, over 90 % effectiveness of

removal of all studied metals. SK and SW provided slightly lower results (80 % and more), however, as mentioned above, uncertainty of determination of the studied metals is 10 %, which is illustrated by error bars. It should be assumed that, due to the content of organic substances in eggshells, the progress of the process: $CaCO_3 \leftrightarrows Ca^{2+} + CO_3^{2-}$ may be less effective which, in turn, influences the hydrolysis process and generation of insoluble hydroxides and carbonates of the studied heavy metals.
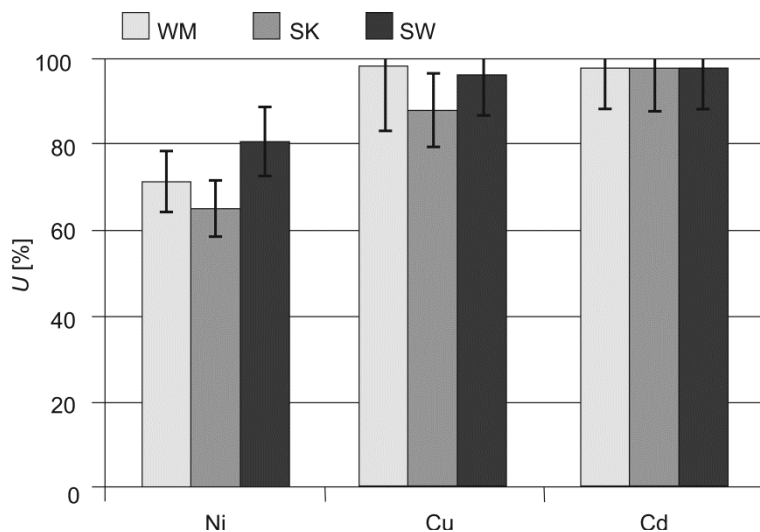
Fig. 3.  Effectiveness of nickel, copper and cadmium cations removal from Solution II (Table 2) with the use of WM, SK and SW
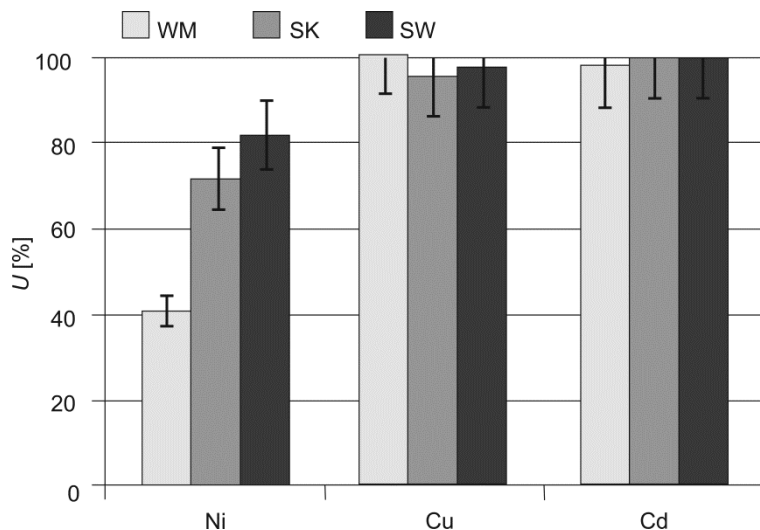
Fig. 4.  Effectiveness of nickel, copper and cadmium cations removal from Solution III (Table 2) with the use of WM, SK and SW

The results presented in Figure 2 indicate that with metal concentrations not exceeding 0.04 mmol/dm$^3$, nickel cations removal effectiveness decreases by the values higher than the determined values of measurement uncertainty.

The comparison of the data presented in Figures 2-4 indicates that with increased initial concentrations of Ni, Cu and Cd cations, the effectiveness of Ni cations removal decreases, in comparison to other metal cations. The differences in effectiveness of nickel removal by WM, SK and SW from Solution III were also demonstrated. Much lower effectiveness of Ni removal, in comparison to SK (approx. 70 %) and SW (approx. 80 %), was registered in the case of using clay limestone (approx. 40 %).

The data from literature, related to the use of hen eggshells use in removing heavy metal cations from solutions, confirm effectiveness of the method. It was demonstrated that, among others, at initial concentrations of the cations: Cu, Cd and Pb in a solution of 10 mg/dm$^3$ (pH approx. 5.5), removal effectiveness was close to 100 % and was decreasing with the increase of initial concentration of metal cations in the solution, which is in accordance with the presented study results. For the initial metal cations concentrations $c_{Cu}$ = 60 mg/dm$^3$ (0.94 mmol/dm$^3$), $c_{Cd}$ = 60 mg/dm$^3$ (0.53 mmol/dm$^3$) and $c_{Pb}$ = 150 mg/dm$^3$ (0.72 mmol/dm$^3$), the removal effectiveness decreased to approximately 85, 21 and 79 %, respectively [33]. Detailed studies on the effectiveness of Ni and Ag cations removal from solutions, with the use of eggshells divided by shells with organic membrane, shells without membranes and membranes alone, demonstrated that the removal effectiveness decreases along with the increase of the initial concentration of metal cations in the solution [34]. Moreover, it was demonstrated that removal effectiveness depends on the contact time, the relation $V/m$, where: $V$ - a solution volume, $m$ - shells mass, a solution temperature and pH. It was demonstrated that under shell membranes have very good sorption characteristics, which improves effectiveness of metal cations removal.

However, it should be emphasised that comparing the values $U$ (relation (3)), which are relative, presents a view on the treatment effects, but it does not indicate the process effectiveness in the absolute sense. For example, for the solutions I-III, the effectiveness of copper removal by SK was approx. 90 %, whereas, taking into consideration the initial concentrations of copper in the solutions (Table 2), the absolute changes of copper cations concentrations decreased for the solutions I-III by, respectively: 0.0063, 0.0346 and 0.0613 mol/dm$^3$.

Relatively highest effectiveness of Ni removal by SW (Figs. 3 and 4) may be justified by, as mentioned before, the largest use of under shell membranes with very good sorption characteristics [34]. The process of hydroxides generation during the process of the studied metal cations removal is confirmed by the solutions pH measurements results. Regardless of the calcium carbonate source (WM, SK or SW), the final pH values of solutions were decreasing, along with the increase of initial metals concentrations in the solution, which also indicates a chemical reaction, which generates insoluble hydroxides.

## Conclusions

The carried out research demonstrated that hen eggshells can be successfully used as a substitute of clay limestone in removal heavy metals from waste water in wet flue gas desulphurisation installations. This is of considerable importance, as the shells have been treated as a waste product so far. It has also been demonstrated that the dominating mechanism of metal cations removal is their precipitation in the form of hydroxides and

carbonates, however, the process of removal with the use of shells may also undergo as a result of ions exchange on the organic compounds of the shells, particularly in under shell membranes.

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