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Separation of Cu(II) ions from synthetic solutions and wastewater by raw and calcined seashell waste

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ABSTRACT

The limestone and lime are agents widely used for separation of toxic metals from contaminated water. To reduce the exploitation of natural limestone deposits, appropriate replacements are sought out among the waste materials and by-products. Seashells, accumulated as an abundant waste in coastal areas, have high content of calcium carbonate and so far have shown high efficiency in neutralization and metal immobilization processes. In this study, the removal of Cu(II) ions was investigated using grounded seashell waste (a) without any pretreatment and (b) exposed to temperature treatment in the range 300–900°C. The influence of temperature on the mineral phase transformation, solution pH and the removal efficiency of Cu(II) ions was monitored. Treatments at $T > 500°C$ exhibit positive effect on Cu(II) separation, with the samples partially or completely converted to calcium oxide being the most effective in the entire Cu(II) concentration range (6.34–639 mg/L). The efficiency of Cu(II) removal was largely associated with the effect on solution pH. The two level full factorial design was used to evaluate the significance of seashell composition (calcium carbonate vs. calcium oxide), granulation, dose and contact time, on the separation of Cu(II) and other cationic pollutants (Fe, Zn, Ni and Pb) from wastewater. The seashell dose and granulation, as well as their interaction, were generally the most influential factors. The variations in the levels of investigated factors had a substantial effect on the process through the indirect effect onto the solution pH. More than 99% of Cu(II) ions were separated at $pH > 7$, while the final pH range 8.2–12.2 was found optimal for total metal separation (97.6–98.9%).

Keywords: Seashell waste; Temperature treatment; Cu(II) removal; Wastewater treatment; Experimental design

1. Introduction

Metal-contaminated wastewater treatment is based on a variety of physico-chemical [1,2] and biological methods [3]. The key factors in selecting the most effective treatment are initial metal concentration, performance of treatment process, simplicity and flexibility of the plant, economics parameters and environmental impacts. Recent developments in toxic metal removal from industrial wastewater are focused on innovative physicochemical processes: adsorption on new adsorbents, membrane filtration, electrodialysis, and photocatalysis [4]. New adsorbents are the most frequently studied and also widely applied. To ensure the economic viability of treatments, the efforts have been made to select a proper adsorbent material among low cost and easily accessible natural geological materials [5], waste and by-products [6].

Considering metal separation, a systematic inventory of relevant published reports has disclosed an important

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position of limestone among natural minerals [7]. Removal of toxic metals (Pb, Cu, Cd, Zn, Cr, Hg, etc.) by natural limestone is based on several binding mechanisms including adsorption, ion exchange and precipitation. In addition, limestone is the raw material used for production of lime – the most commonly employed agent for the adjustment of pH to the basic conditions which enable heavy metal removal by chemical precipitation. In spite of recognized disadvantages of a precipitation process, such as the consumption of large amount of chemicals, production of sludge that requires treatment and disposal, poor settling, etc., lime precipitation is one of the most effective ways to treat effluents with high metal concentration (>1000 mg/L) [4].

Due to the large consumption of natural limestone, alternative sources of calcium carbonate ($CaCO_3$) are being investigated, such as the shells of snails [8], marine organisms [9], and egg shells [10]. Seashell farming is a particularly fast developing industry accompanied by the increased amount of generated and disposed waste shells [11]. During natural decomposition of seashell organic material a lot of smelly and, in some cases toxic compounds are produced, therefore, the utilization of waste shells affects the quality of the coastal environment.

The prospect of using seashell waste to sequester toxic metal species from aqueous solutions was investigated in the range of experimental conditions. The difference between aragonite and calcite based shells was analyzed in respect to Pb, Zn and Cd removal [12], as well as the affinity of different structural layers of seashell towards Cu ions [13]. The effect of process parameters (such as the time of reaction, metal concentration, sorbent dose, presence of cationic and anionic chemical species, etc.) has been analyzed in respect to numerous toxic metals and radionuclides including Pb and Cu ions [14,15], Ni, Cs, Co [15], Cr [16], Cd [17] and Hg [18]. To facilitate the prediction of cation removal efficiency taking into account the process specific, metal specific parameters and their non-linear interactions, the model based on general regression neural network (GRNN) architecture was developed [19]. Recent batch and column studies showed a great potential of seashell derived adsorbent in the treatment of complex wastewater, i.e., acid mine drainage (AMD) [20]. Moreover, application of mussel shells as alkalinity-generating material in sulfate-reducing bioreactors (SRBRs), was more effective than application of a limestone, with a higher alkalinity generation and a better metal removal from AMD [21].

Previous study has shown relatively small capacity of seashell waste in separation of Cu(II) ions, when compared to the removal efficiency of Pb(II), Zn(II) and Sr(II) [19]. Removal of metal cations is commonly followed by the crystallization of carbonates of the metals to which the seashells were exposed, i.e., strontianite – $SrCO_3$, hydrozincite – $Zn_5(CO_3)_2(OH)_6$, cerussite – $PbCO_3$ [19] and otavite – $CdCO_3$ [17] were detected by means of X-ray diffraction (XRD) analysis. However, the uptake of Cu(II) ions did not cause changes in the original seashell structure of both aragonite [19] and calcite type [13]. Even at maximum saturation loadings, the amount of Cu(II) in seashell material was insufficient to form a new phase detectable by XRD. In relation to other investigated metals, sorption of Cu(II) was the fastest, with the lowest maximum capacity of sorption and the most pronounced decrease in equilibrium pH in respect to the amount of metal sorbed [19].

Various chemical treatments can enhance the capacity of seashells for Cu(II) removal. Treatment of bivalve mollusk shells by acidic solution was found to increase Cu(II) sorption capacity due to occurrence of organic functional groups (–OH, –NH, C=O and S=O) at the surface, which can directly bind metal ions [22]. Alkaline treatment with sodium hydroxide (NaOH) solution also improved Cu(II) removal, creating deficiency in positive surface charge by Ca/Na replacement over the outer layers of aragonite [23]. The effect of temperature treatment of seashell waste onto Cu(II) removal has not been considered, still, calcination of shells was found to increase the efficiency of removal of some metals, such as Hg [18].

In the present study, the effect of seashell temperature treatments onto Cu(II) separation was investigated using synthetic single-component and real wastewater. Crushed seashells were annealed to different temperatures in the range 300°C–900°C, while changes in mineralogical composition and the effects on metal removal were monitored. The removal of Cu(II) and other cationic pollutants from real wastewater was analyzed by full factorial design, taking into account seashell treatment, granulation, dose and the contact time, as independent process variables. In addition to residual metal concentrations, final pH was the measured system response, and its effect on process efficiency was discussed.

2. Materials and methods

The seashell waste was collected at the North Greek Aegean Sea coast as a composite sample of several bivalvia species characteristic for the region [19]. To remove the particles of sand and soluble impurities, shells were rinsed several times with hot water and then dried at 50ºC. The shells were grounded in the laboratory ball mill and sieved to different particle size fractions.

2.1. Seashell waste characterization

Thermal stability and phase transformation of the seashell waste (denoted SW) have been monitored by the static method of thermal analysis. Precisely measured portions of SW (10.000 g), with particle size 0.4–1 mm, were annealed in the electrical furnace in ambient air, at the constant temperature for 4 h. The investigated temperature range was 300–900ºC. After cooling the samples (denoted SW300 – SW900) in the desiccator, the weight was measured again and the percentage of weight loss was calculated for each temperature. All treatments were performed in duplicate, with final values taken as the mean value of two measurements.

An X-ray diffraction analysis was used for monitoring the changes in the mineralogical composition caused by annealing. Rigaku Smartlab SAXS diffractometer was used within 10–60 2θ range, with 0.05 step size and dwell time of 2.0 deg/min.

2.2. Separation of metal cations from synthetic and real wastewater

The potential of differently treated SW samples to remove metal cations from aqueous solutions was examined in batch mode, at room temperature (21 ± 2ºC), using both synthetic and real wastewater.

2.2.1. Separation of Cu(II) ions from synthetic wastewater

Samples SW, SW300 – SW900 were mixed with Cu(II) solutions in 50 mL centrifuge tubes, which were agitated using an overhead laboratory shaker (Heidolph, Reax 20) set at 10 rpm. Working solutions were prepared from copper(II) nitrate 3–hydrate ($Cu(NO_3)_2 \times 3H_2O$; p.a. Across Organics) and deionized water. The initial Cu(II) concentrations were 6.34 mg/L, 63.8 mg/L and 639 mg/L, whereas the initial pH value was adjusted to 5.0 ± 0.2 using 0.01 mol/L solutions of either NaOH or HNO_3. The seashells were applied at the dose of 5 g/L, while the contact time was fixed at 24 h. In addition, the series of blank experiments were conducted under the same experimental conditions using deionized water instead of metal containing solutions, in order to determine and compare the aqueous pH values of different seashell samples. Duplicate experiments were performed for each set of conditions, and average results are presented.

Table 1
Analyzed process factors and their levels

Factor		Level –1	Level 1
A	Seashell waste type	SW	SW900
B	Particle size (mm)	<0.2	0.4–1
C	Reaction time (h)	1	5
D	Seashell dose (g/L)	15	50

2.2.2. Separation of Cu(II) and other metal cations from real wastewater

The sample of wastewater (WW) was collected at the Mining and Smelting Basin (RTB) Bor (Serbia). The waste streams generated by the copper smelting process are characterized by low pH, high content of sulfate anions and high concentrations of metals, particularly Cu, Zn and Fe [24]. To facilitate the analysis of different factors that influence metal removal, and to enable the calculation and comparison of their effects, experimental design methodology (DOE) was applied [25]. Taking into consideration four process variables at two levels (Table 1), the full factorial design matrix was constructed (Table 2). The type, the granulation and the dose of seashell waste, as well as the contact time with WW, were selected independent process variables. Based on the results of previous characterization, untreated SW (carbonate) and SW treated at 900°C (completely converted to calcium oxide), were selected as representative sample types and prepared at two different granulations. Percentage of metal removal and pH value at the end of each experiment were the measured responses. Appropriate amount of SW or SW900 was shaken with fixed volume of WW (20.00 mL) in 50 mL Erlenmeyer flasks, on an orbital laboratory shaker (120 rpm).

After each set of sorption experiments, from either synthetic solutions or wastewater, separation of the

Table 2
Description of the level of factors in each experiment according to the matrix of full factorial experimental design and the measured system responses

No.	Seashell type	Particle size (mm)	Contact time (h)	Seashell dose (g/L)	Final pH	Removal efficiency (%)				
						Cu	Zn	Fe	Pb	Ni
1	SW	<0.2	5	15	6.06	46.6	5.53	98.5	78.3	1.82
2	SW900	0.4–1	1	50	12.81	99.9	92.2	98.6	76.9	40.9
3	SW	0.4–1	5	50	6.13	75.0	5.42	98.5	76.3	3.18
4	SW	0.4–1	5	15	2.33	0.00	0.00	0.90	22.1	3.86
5	SW	0.4–1	1	50	6.36	50.9	8.58	98.6	73.0	4.55
6	SW900	<0.2	5	15	12.26	99.9	98.1	98.6	75.1	41.6
7	SW900	0.4–1	5	15	3.09	0.00	0.00	1.95	11.3	2.95
8	SW	<0.2	1	50	7.60	99.9	50.0	98.6	74.6	7.73
9	SW	0.4–1	1	15	2.14	1.14	3.34	9.63	16.4	3.64
10	SW	<0.2	1	15	5.99	34.7	0.00	98.6	71.2	8.41
11	SW	<0.2	5	50	8.25	99.8	94.0	98.7	72.8	7.95
12	SW900	<0.2	1	50	12.80	99.1	90.7	98.6	61.7	40.2
13	SW900	0.4–1	1	15	2.22	2.28	0.74	3.85	5.30	4.32
14	SW900	0.4–1	5	50	12.71	99.9	95.9	98.6	70.3	40.7
15	SW900	<0.2	1	15	6.07	73.6	14.8	98.5	71.0	8.41
16	SW900	<0.2	5	50	12.64	99.9	94.8	98.7	67.0	42.3

liquid and solid phase was done by centrifugation by Hareaus Megafuge 16 (10 min., at 9000 rpm). The pH of clear supernatant was measured using InoLab WTW pH meter. Measurements of the initial and residual metal concentration were conducted using Perkin Elmer 3100 Atomic Absorption Spectrophotometer.

3. Results and discussion

Temperature treatments induced a weight loss and mineralogical transformation of SW, which influenced the removal of Cu(II) and other metal cations from synthetic solutions and the real wastewater.

3.1. Weight loss and mineralogical transformation of SW as a function of temperature

The relative weight of shells in the investigated temperature range and the corresponding mineral phase transformation are shown in Figs. 1 and 2.

The determination of SW mineralogical composition has revealed calcium-carbonate phase crystallizing within orthorhombic crystal system *P m c n* characteristic for aragonite polymorph [19]. The overall weight loss of 3.3% detected up to 600ºC may be contributed to the content of organic matter (Fig. 1). The dark color of samples SW500 and SW600 also indicates thermal decomposition of organic constituents. As the temperature increased over 600ºC, the decomposition of $CaCO_3$ phase to calcium oxide (CaO) and carbon dioxide (CO_2) occurred according to the reaction:

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \tag{1}$$

The weight loss of 45.1 ± 1.2% was detected at 900ºC. The results are in line with the behavior of geological $CaCO_3$ [26], as well as of other seashell waste [27], however, the temperature of dissociation is not constant for different specimens, due to variable grain size and presence of impurities.

Aragonite polymorph has been completely transformed to calcite between 300ºC and 400ºC (Fig. 2). For different aragonite specimens, the temperature of transition to calcite was reported to vary between 387ºC and 488ºC [26]. The intensity of calcite peaks started to decrease between 700ºC and 800ºC, while simultaneously, the characteristic diffraction maximums of lime (CaO) increased. At 900ºC only CaO peaks were detected, while the traces of detected portlandite (calcium hydroxide, $Ca(OH)_2$) are most likely a result of surface interaction with atmospheric water upon cooling and storage [28]. The investigated seashell waste represents rich source of $CaCO_3$, comparable to commercial limestone samples [29,30].

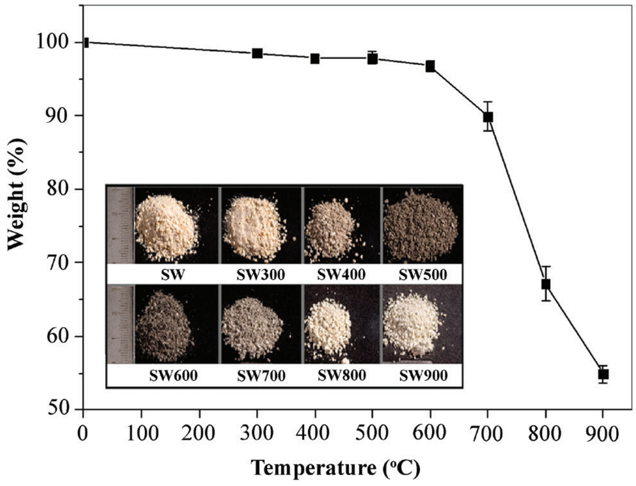

Fig. 1. The weight loss of seashells at different temperatures and the appearance of corresponding powders (insert).

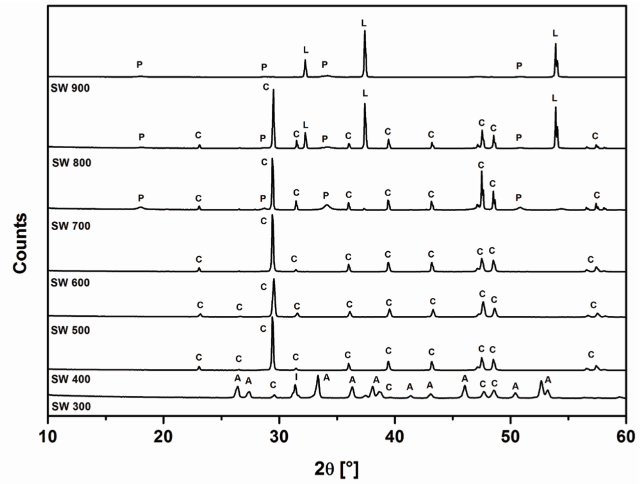

Fig. 2. Powder XRD patterns of SW after heat treatment at various temperatures. The crystalline phases are indicated as follows: aragonite (A – $CaCO_3$), calcite (C – $CaCO_3$), lime (L – CaO) and portlandite (P – $Ca(OH)_2$).

3.2. Effect of SW temperature treatments on Cu(II) removal from synthetic solutions

In Fig. 3a, Cu(II) removal efficiency was compared for differently treated seashell samples and different initial Cu(II) concentrations. Using unprocessed SW, 96.3%, 33.4% and 10.1% of Cu(II) ions were removed from 6.34 mg/L, 63.8 mg/L and 639 mg/L solutions, respectively. Under equivalent experimental conditions, small fluctuations in removal efficiency were observed using samples heated up to 500°C, with the slight decrease in the batches containing SW400 and SW500 and more concentrated Cu(II) solutions. Using SW600, Cu(II) removal from 639 mg/L solution increased to 22.8%, while from 63.8 mg/L abruptly increase to 90.9%. Finally, mixing of samples SW700, SW800 and SW900 with synthetic wastewater led to a high percentage Cu(II) removal in the entire range of concentrations (91.2–99.9%). Considering samples SW800 and SW900, higher percentage removal was observed for higher initial Cu concentrations (Fig. 3a), nevertheless, final Cu(II) concentration was in the range 0.44–1.00 mg/L for all studied initial concentrations.

Temperature induced alteration of SW mineralogical composition displayed effects in terms of material solubility and pH. In the series of blank experiments conducted by adding various seashell samples into deionized water, final solution pH varied in the range 9.5–12.8 (Fig. 3b). The observed increase in pH is in agreement with the $CaCO_3$ to CaO conversion. Exothermic reaction of calcium oxide with water results in formation of calcium hydroxide ($Ca(OH)_2$), with the solubility product ($K_{sp} = 5.5 \times 10^{-6}$), high enough to produce an alkaline pH.

Solution pH was also influenced by the concentration of Cu(II) ions. After reaction of SW, SW300–SW600 with 6.34 mg/L Cu(II), final pH values were for 0.1–0.6 pH units lower when compared to the blank experiment. With the increase in Cu(II) content, final pH decreased notably, reaching 6.4–6.9 for 63.8 mg/L and 5.8–5.9 for 639 mg/L synthetic solution. Samples SW700-SW900 exhibited alkaline pH upon reaction with Cu(II) solution (final pH 12.4–12.8), with an exception of final pH 7.7 in the system SW700/639 mg/L Cu(II). This decrease in final pH could be explained by reactions of Cu(II) complexation with protonated surface groups according to the following equations:

$$2S\text{–}OH + Cu^{2+} \rightarrow (S\text{–}O)_2Cu + 2H^+ \tag{2}$$

$$S\text{–}OH_2^+ + Cu^{2+} \rightarrow S\text{–}OCu^+ + 2H^+ \tag{3}$$

where S–OH and $S\text{–}OH_2^+$ represent neutral and positively charged groups on the surface (S).

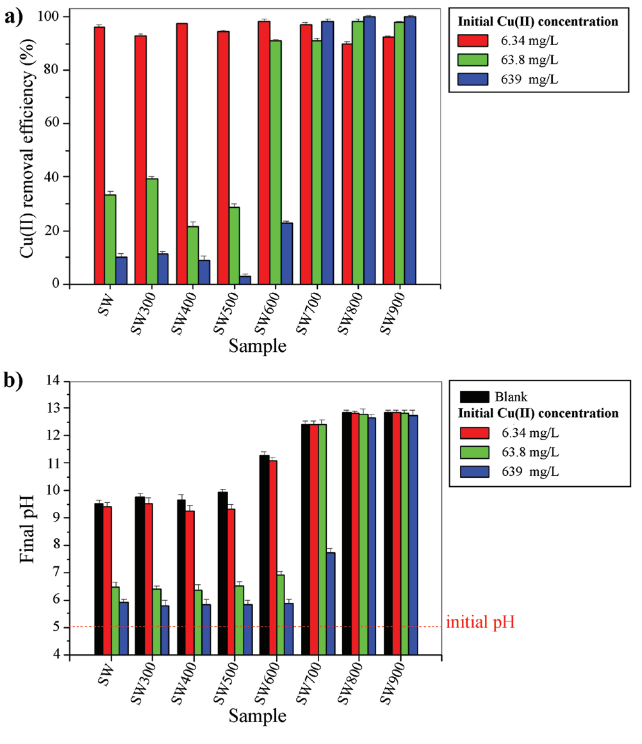

Fig. 3. Effect of SW temperature treatment and initial Cu(II) concentration onto (a) Cu(II) removal efficiency and (b) final pH of the solution (seashell dose 5 g/L, contact time 24 h).

The differences in the Cu(II) removal capacity between carbonate-based samples SW300, SW400, SW500 and SW600 coincide with several observed changes in material properties: the complete transition of SW structure from aragonite to thermodynamically more stable calcite polymorph between 300°C and 400°C, the increase in calcite crystallinity and the loss of organic matter with the increase in temperature. Comparison of finely ground mussel shells and the sample treated at 550°C has revealed higher content of calcite in calcined sample, and in the same time, higher capacity to sequester Hg ions [18]. However, even though calcite was the only identified crystalline phase in the samples SW400, SW500 and SW600, their capacity to remove Cu(II) was different. Apparently, besides aragonite/calcite composition, other properties of treated samples, possibly their interactions or synergistic effects, also influenced the chemical reactivity of the residual solids and affected the metal removal. On the other hand, efficient removal of Cu(II) by samples heated over 700ºC is connected with the formation of CaO phase, which provides the pH conditions for Cu(II) precipitation [31,32].

Since the reaction with SW caused drastic change in solution pH and the final pH displayed dependence on SW treatment and Cu(II) concentration (Fig. 3), the relationship between final pH value and Cu(II) removal efficiency was further analyzed. Solution pH has a significant influence on Cu(II) speciation, and the mechanism of its removal. Typically below pH 6, cupric ion (Cu^{2+}) is the preferential soluble form in the absence of anionic ligands, whereas the metal precipitates as copper hydroxide [K_{sp} $Cu(OH)_2 = 10^{-19.32}$] at pH 6.5–12, depending on copper concentration, other anions and cations in the solution, temperature, and time to thermodynamic equilibrium [33]. Regardless of SW composition and Cu(II) concentration, efficient removal was achieved in all batch systems with final pH ~ 7 or higher (Fig. 4). At the lowest (6.34 mg/L) concentration of Cu(II), pH was raised from initial pH 5.0 to pH > 9 using all investigated samples of seashell waste. At higher Cu(II) concentrations (63.8 and 639 mg/L), samples partially and

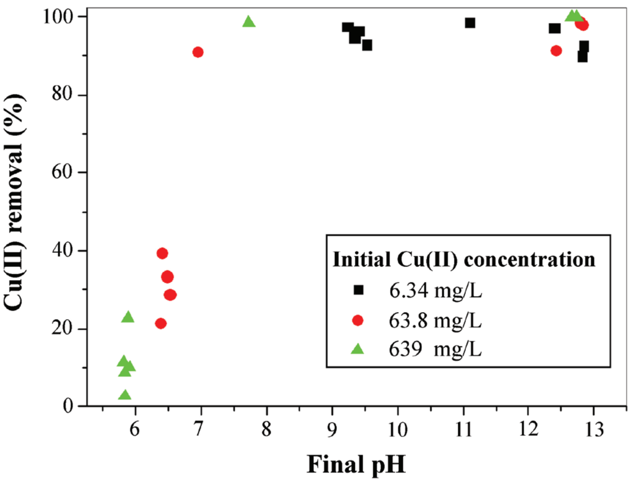

Fig. 4. Relationship between final pH value and removal rate of Cu(II) by untreated and variously treated seashell waste (SW, SW300 – SW900).

completely converted to the CaO (SW700 – SW900) lifted the pH above 7 and enabled efficient Cu removal. Only below critical pH ~ 7, other effects of annealing become apparent causing differences in Cu(II) removal by approximately 20%. Therefore, at this point, the effect of seashell waste annealing on Cu(II) removal appears to be mainly associated with the indirect effect of the material on the solution pH.

It seems important to notice that after exposure of SW900 (fully converted to CaO) to 639 mg/L Cu(II) solution, precipitate color change was observed during the course of the reaction. The blue color of precipitated $Cu(OH)_2$ gradually turned to characteristic dark color of tenorite (copper(II) oxide, CuO), which can be associated with the transformation of a solid from more to less soluble form, with time (insert in Fig. 5). The XRD analysis of such precipitate have confirmed the presence of portlandite ($Ca(OH)_2$), low intensity calcite peaks from the reaction of $Ca(OH)_2$ with atmospheric CO_2, and a new crystalline solid – tenorite (CuO) (Fig. 5).

Spontaneous slow transformation of $Cu(OH)_2$ to CuO is possible at room temperature [31] and the kinetic of transformation was found to be controlled by pH of the system [34]. The proposed mechanism of transformation in alkaline media involves a complex anion $Cu(OH)_4^{2-}$, as a precursor entity for the formation of CuO [35]:

$$Cu(OH)_2\,(s) + 2OH^-\,(aq) \rightarrow Cu(OH)_4^{2-}\,(aq) \leftrightarrow CuO\,(s) + 2OH^-\,(aq) + H_2O \tag{4}$$

The effect of "solid aging" contributes to the stability of immobilized Cu(II) ions, therefore, the process of transformation under different conditions dissevers further investigation.

3.3. Effect of process variables on the removal of Cu(II) and other metal cations from the real wastewater

The analysis of real WW has disclosed Cu(II) as a major contaminant (613.2 mg/L) followed by Zn (270.1 mg/L) and Fe (104.0 mg/L), and low concentrations of Ni and Pb (4.40 and 4.34 mg/L, respectively). The initial pH of WW was 1.6.

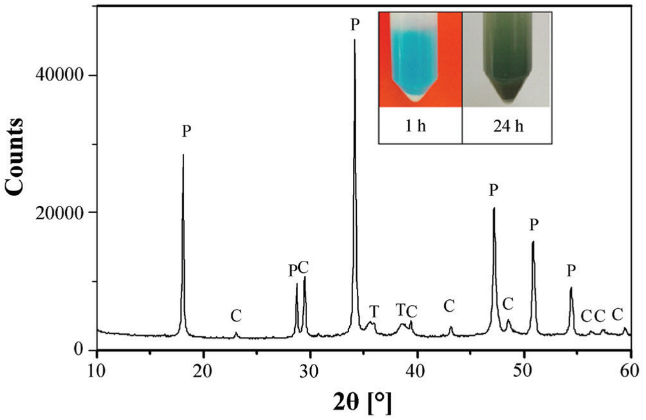

Fig. 5. Diffractogram of sample SW900 after reaction with 639 mg/L Cu(II) solution. Identified crystalline phase: C – calcite ($CaCO_3$), P – Portlandite ($Ca(OH)_2$), T – Tenorite (CuO). Inserted photograph shows the change of color of SW900/Cu suspension during the process.

The results of experiments conducted according to the experimental design matrix are presented in Table 2. Statistical analysis of the data was performed using MINITAB software. The change in a measured system response caused by the change in the variable level is defined as the effect of variable [36]. Furthermore, an interaction between the factors is detected if the difference in response between the levels of one factor is not the same at both levels of another factor. Interactions can significantly increase or decrease the main effects.

Visualization and understanding of the effects of different factors is facilitated using the graphical display of the data. In this study, main effect plots were created to analyze and compare the effects of chosen variables on different system response. The reference horizontal line on the main effect graph represents the overall mean. Therefore, the greater the magnitude of the main effect - the steeper the slope of the line connecting the response mean for each factor level. Furthermore, if the factor has a positive effect, it produces the increase in response when the settings change from its low to its high level. Conversely, negative value of effect denotes decrease in system response with the change of factor level from low to high.

The normal probability plots were used to determine the magnitude and the direction of all effects (including interactions), and to gain information of their statistical significance. Normal probability plot shows the effects in relation to the distribution fit line for the case when all the effects are 0. In order to be statistically significant, the effect of a factor must be on a certain distance from the reference line, which depends on the significance level (denoted by α).

In the present study, the chosen confidence interval was 95% ($\alpha = 0.05$), and the results for different system responses are summarized in Figs. 6 and 7.

It can be observed from Fig. 6 that measured responses were largely influenced by variation of investigated factors. The increase in seashell dose had a pronounced positive effect on metal removal and the final pH, while the effect of variation of particle size from finer to coarser granulation was commonly negative. The switch between two seashell types (SW and SW900) has demonstrated the effects of different intensities and directions on the examined system responses. Application of SW900 led to more efficient separation of Cu, Ni and Zn and higher final pH. Contrary, Pb removal was more pronounced using untreated SW, while the type of seashells had virtually no effect on Fe removal. Finally, the effect of prolonged reaction time on Fe removal was negligible, while slightly positive considering other system responses. In comparison with other effects, variation of time of contact was the least significant. Its highest positive effect is observed for Zn removal efficiency as a response.

Normal probability plots (Fig. 7) show that only a few main effects were statistically significant, while, on the other hand, the significant interactions are revealed. The removal of Cu(II) ions was under a complex influence of several factors and their interactions. Main effects statistically important for Cu removal were seashell dose (D), granulation (B) and type (A). Cu(II) removal efficiency increases with the increase in seashell dose, using SW900 instead of SW and using

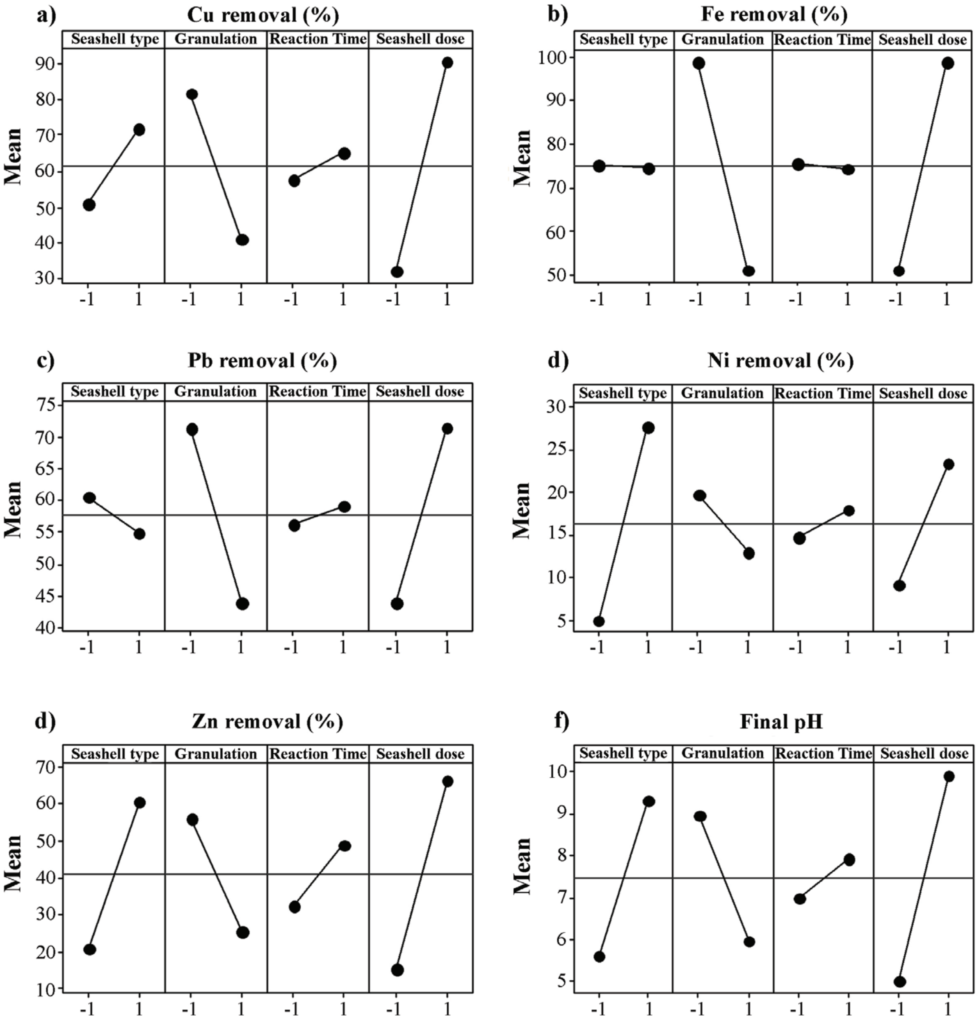

Fig. 6. Main effect plots for the following system responses: a) Cu removal (%), b) Fe removal (%), c) Pb removal (%), d) Ni removal (%), e) Zn removal (%) and f) final pH.

finer granulation of the materials. The BD interaction was significant, as well as the three-way ABD interaction.

Similarly, significant positive effects of the factor D and BD interaction, and negative effect of factor B were determined for Fe and Pb removal (Figs. 7b and 7c). Effect of variation of the type of seashell was also significant for Pb and Ni removal, with opposite directions. Although the changes in factor levels drastically altered the degree of Zn separation from WW, none of the effects was statistically significant at chosen confidence interval (Fig. 7e).

After each treatment, the pH of WW increased, but to a different point depending on the level of the factors. The significant factors with positive effects were seashell type and dose (Fig. 7f), i.e. using the SW900 at higher dose produced the highest shift in pH. Finally, the time of contact had no statistical significance on any of the responses.

The BD two-way interactions were additionally analyzed by construction of interaction plots (Fig. 8), due to their statistical significance. A common conclusion arising from three graphics is that the effect of variation of sorbent dose is more important for coarser than for finer fraction of seashells.

If the efficiency of metal removal is displayed as a function of the pH recorded at the end of each experiment, the relationships shown in Fig. 9 are obtained. Overall metal removal is insignificant in the pH range 2–3. As the pH increases, the fraction of cations removed from the WW also increases. The percentage of removed Fe rose most steeply, followed by Pb, Cu, Zn and finally Ni. This trend follows the trend of changes in the first hydrolysis constant (p*K*a) of the cations under consideration (Fe^{3+} (2.2) < Pb^{2+} (7.7) < Cu^{2+} (8.0) < Zn^{2+} (9.0) < Ni^{2+} (9.9) [37]), confirming the importance of final pH in the process. Correspondingly, the efficiency of steal slag in separation of aqueous metal cations was associated with its ability to increase the pH and enable formation of insoluble species of selected metals [38].

As in the study of Cu(II) removal from synthetic single-component solutions, more than 99% of Cu(II) ions were separated from WW at pH > 7. Zn ions were separated to the largest extent (94.8–98.1%) in the pH range pH 8.2–12.2. Removal of minor constituents have reached maximum of 70% for Pb in the pH range 6–12.2, and approximately 40% for Ni at pH 12.2–12.8. Removal of minor constituents of

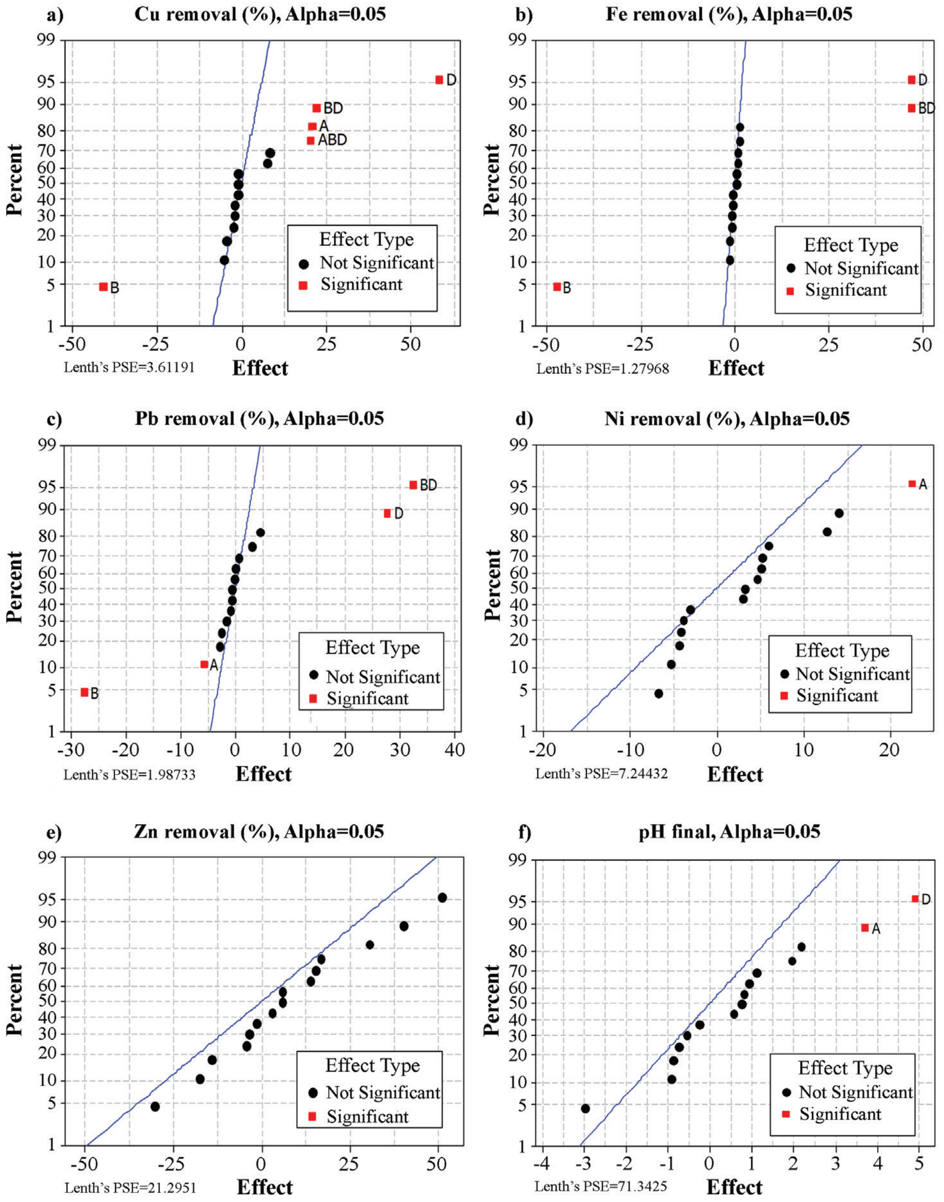

Fig. 7. Normal probability plots of the effects of process factors onto: a) Cu removal (%), b) Fe removal (%), c) Pb removal (%), d) Ni removal (%), e) Zn removal (%) and f) final pH. Process factors: A – Seashell type, B – Granulation, C – Reaction time, D – Seashell dose.

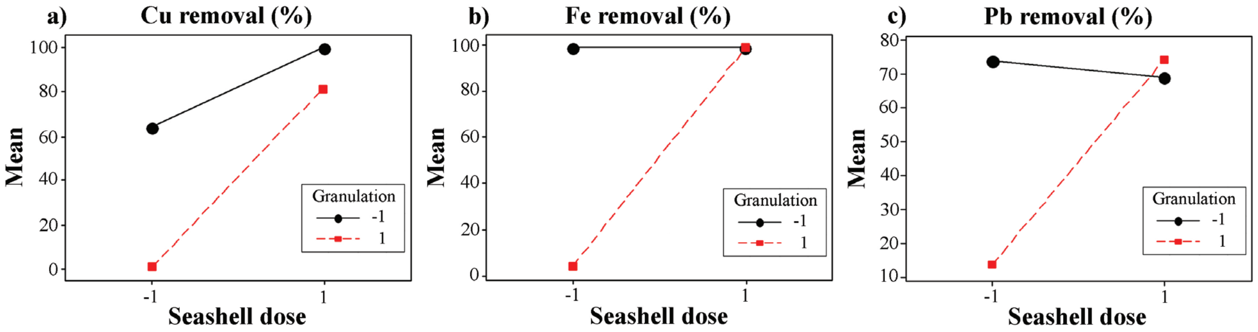

Fig. 8. Two-way interaction effect of seashell dose and granulation onto removal efficiency of Cu ions (a), Fe ions (b) and Pb ions (c).

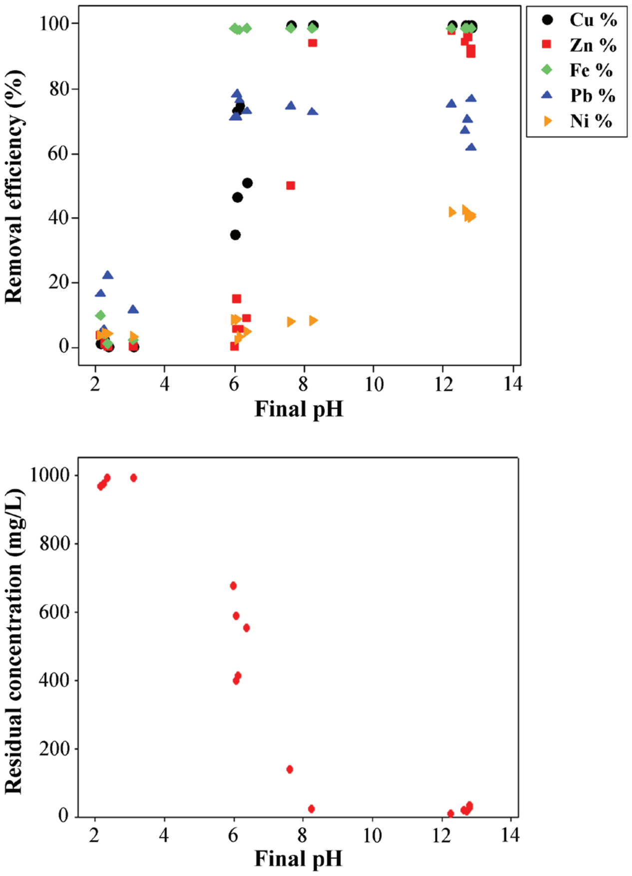

Fig. 9. (a) Efficiency of metal removal from wastewater, and (b) total residual concentration of metals, as a function of final pH (experimental conditions are given in Table 2).

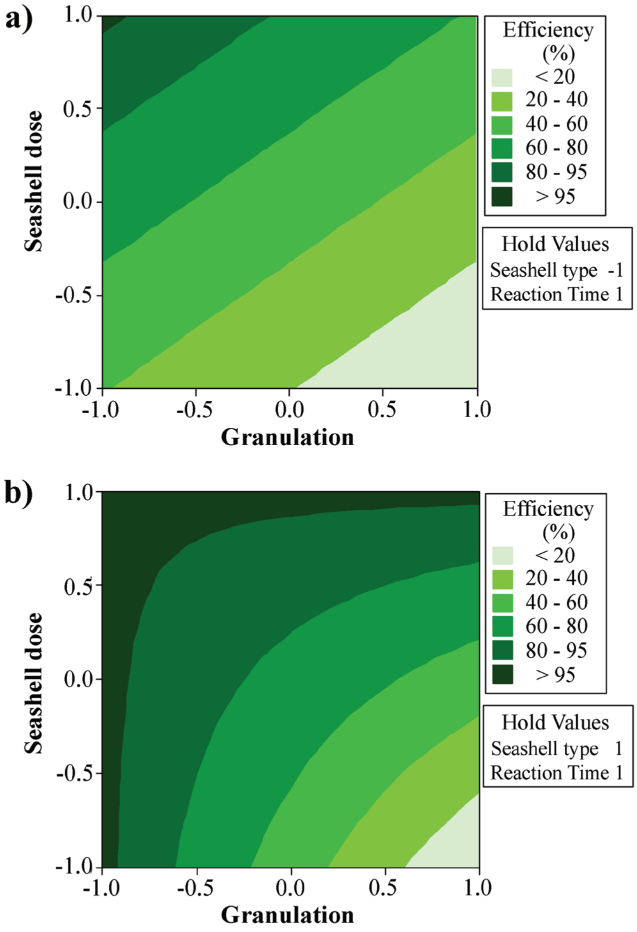

Fig. 10. The contour plots showing the overall efficiency of WW treatment achieved by varying dose and granulation of (a) SW and (b) SW900, at the fixed contact time (5 h).

WW was affected by competition, and additionally Ni(II) ions was the most difficult to remove since they precipitate at the highest pH values.

Pb(II) and Zn(II) compounds were partially re-dissolved at pH > 12.2, most likely due to formation of $Pb(OH)_3^-$ and $Zn(OH)_3^-$ complexes. Therefore, the final pH range 8.2–12.2 was optimal (97.6–98.9%) for total metal removal from WW (Fig. 9b).

The complex effects of variables and their interactions may be well perceived by constructing the contour plots which display the overall efficiency of WW treatment achieved at the fixed contact time using different combinations of granulation and dose of untreated SW (Fig. 10a) and SW900 (Fig. 10b). Removal of more than 95% of all metal cations can be reached only using fine granulation of SW at high dose level. Contrary, addition of SW900 can provide the same results at a range of granulation/dose combinations.

4. Conclusion

The seashell waste was submitted to temperature treatments from 300°C to 900°C in order to evaluate the effect of temperature on the material`s ability to sequester Cu(II) ions. Tested samples were equally effective in removing Cu(II) from a low concentration single component solution (6.34 mg/L), while differentiation was observed at elevated concentrations (63.8 and 639 mg/L). The transition of aragonite to calcite polymorph between 300°C–400ºC, the increase of calcite crystallinity and the loss of organic phase up to 600°C have displayed disparate effects on metal removal. Treatments at higher temperatures enabled efficient Cu(II) removal due to calcite decomposition to CaO. Correlation of the achieved purification effects with the final values of solution pH have revealed almost complete Cu(II) separation in each system with pH > 7, regardless of the composition of the seashells and Cu(II) concentration. The applied full factorial experimental design underlined the significance of different process parameters onto the efficiency of removing cationic pollutants (Cu, Fe, Zn, Pb and Ni) from wastewater, the total process efficiency, and the final pH. Cu(II) removal was found significantly (α = 0.05) influenced by variations of seashell composition, granulation and dose, as well as by their interactions, whereas the effect of contact time was less important. The application of high level dose and low level granulation of the shells was preferred, as was the application of shells treated at 900ºC in respect to untreated ones. The pH in the system was most affected by the dose and the type of used shells. The effect of investigated factors and their interactions on the overall water purification process was hugely reflected through the change in pH. The use of finely grounded raw shells is simpler and more economical, however, smaller quantities of calcined shells are needed to achieve the optimal pH which will in turn result in smaller amounts of secondary solid waste.

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