Study on effectiveness of PVC/β-diketone sorbent in removing residue of Zn(II), Cr(III) and Ni(II) from post-galvanic wastewater

Katarzyna Witt*, Elżbieta Radzymińska-Lenarcik

Faculty of Chemical Technology and Engineering, UTP University of Sciences and Technology, Seminarjna 3, PL-85326 Bydgoszcz, Poland, Tel. +48-052-374-9001; Fax: +48-052-374-9005, emails: Katarzyna.Witt@utp.edu.pl (K. Witt), elaradz@utp.edu.pl (E. Radzyminska-Lenarcik)

Received 17 September 2019; 4 November 2019

Abstract

Effectiveness of polymer inclusion membranes and polymer sorbents in cleansing post-galvanic wastewater containing Zn(II), Ni(II) and Cr(III) ions have been compared in this paper. Both the membrane and the sorbent were based on polyvinyl chloride (PVC), and 3-propyl-pentane-2,4-dione was applied as the active substance. Using the membrane techniques 75%–78% of zinc and 62%–64% of chromium may be recovered, while in the sorption process it may be 97%–99% of zinc and 95%–98% of chromium. Sorption capacity of the studied composite for Zn(II) and Cr(III) was 59.8 and 37.5 mg/g, respectively. In membrane transport, the values of the Zn/Cr separation coefficient are equal to 1.23 and 1.17, respectively, for zinc and nickel-chromium wastewaters, whereas in the case of the sorption process the value is 1.61. It was shown that sorption on 3-propyl-pentane-2,4-dione modified sorbent is a more efficient method of heavy metal ion separation from post-galvanic wastewater.

Keywords: Heavy metal removal; Post-galvanic wastewater; β-diketones; Polymer inclusion membrane; Sorption

1. Introduction

Along with the improvement of the living standards of society, waste generation resulting from people's social and industrial activity is becoming a serious problem. Waste that contains heavy metals are particularly hazardous.

Separation and selective release of metal ions from water solutions constitute an important technological problem. Both the ecological and economic aspects force scientists to seek more effective methods of separation.

Mostly cheap and ecological methods have been promoted in recent years as ways of heavy metal removal from various environmental elements, including wastewater. Such methods include membrane processes and sorption on various types of sorbents.

In 1993, porous polymer material for removal of metal ions from solutions was produced; it consisted of polyvinyl chloride (PVC), plasticizer, propellant - perhydrol and dust from mixed waste [1]. From that moment, polymer modification has constituted an inexhaustible subject of research on its wide range of applications, also to cleanse wastewater of heavy metals. For example, Elhalawany et al. [2] described chelating polymers (CPs) based on waste polystyrene functionalized by itaconic acid moieties in the absence and presence of montmorillonite clay. These CPs have been used as adsorbents for the removal of different toxic metal ions from their aqueous solutions [2]. In turn, Lalita et al. [3] proposed a synthesis of graft copolymers of chitosan with N-isopropylacrylamide and binary monomers for the removal of Cr(VI), Cu(II) and Fe(II) metal ions from aqueous solutions [3]. PVC promoted with acetylacetone (acac) was successfully used to remove Zn(II), Cu(II) and Pb(II) ions from model solutions reaching, respectively, 91%, 85% and 50% reduction in their concentration at pH = 8.0 [4]. However,
for many years simpler methods of synthesis of specialized polymers that show higher affinity and selectivity of metal ion binding have been sought for. An example of such a simple solution is polymer inclusion membranes (PIM) that are obtained by dissolving a polymer with a compound with functional groups capable of binding metal ions [5–7]. Most of PIM studies used cellulose triacetate (CTA) [8,9] and PVC [10,11] as the base polymer.

The possibility of applying PIMs and polymer sorbents in cleansing post-galvanic wastewater that contains Zn(II), Ni(II) and Cr(III) ions have been investigated in this paper. Both the membrane and the sorbent were based on PVC, and 3-propyl-pentane-2,4-dione was applied as the active substance. The processes were conducted for 8 h, at room temperature. In the studies on transport across PIMs, coefficients of metal recovery were determined, and the process of sorption was characterized by determining sorption capacities. The studies were conducted on three types of post-galvanic wastewaters - zinc, nickel, and nickel-chromium, obtained after an initial process of cleansing (precipitation with milk of lime). The effectiveness of these two methods was compared.

2. Experimental

2.1. Reagents and procedure

2.1.1. Preparation of sorbent modified by 3-propyl-pentane-2,4-dione

The sorbent was prepared from PVC granulate purchased from the SoloStocks Company, Spain. The parameters of PVC granules were as follows: density of 1.24 g/cm³, Shore hardness of 55, tensile strength of 8.7 MPa, elongation at break of 355%, diameter of approx. 4 mm. The PVC granules were mixed with 0.05 mol/L 3-propyl-pentane-2,4-dione solution in kerosene (Chempur Company, Piekary Śląskie, Poland) within 12 h, and they were subsequently dried for 24 h. The amount of adsorbed PVC sorbent was determined using the gravimetric method.

2.1.2. Preparation and characterization of a polymer inclusion membrane doped with 3-propyl-pentane-2,4-dione (carrier)

The polymer membrane was prepared according to the procedure reported in our previous papers [13]. PVC in suspension with an average molecular weight of 72,000 was obtained from the ANWIL Company, Wloclawek, Poland. Analytical grade di(2-ethylhexyl) adipate (DAO) and tetrahydrofuran (THF) were purchased from POCH and used without further purification. The concentration of the carrier (3-propyl-pentane-2,4-dione) in the membrane was 60% since earlier studies indicate that this concentration is optimum for that group of carriers. Organic solutions of the 35% support (PVC), 60% carrier (3-propyl-pentane-2,4-dione), and 5% plasticizer (DAO) were prepared in THF. The obtained mixtures were poured out on an ANUMBRA self-leveling dish with a 6.0 cm diameter. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water.

The thickness of the PIM was measured using a digital micrometer (Panametrics® Magna-Mike® 8500, San Diego, CA, USA) with an accuracy of 0.1 µm. The thickness of a membrane was measured 10 times for each case and shown as the average value of these measurements, with a standard deviation below 1%. The thickness of the membrane before and after transport was found to be the same. The average PIM thickness varied within the range of 28–32 µm.

A surface characterization study of the polymer membrane was performed using an atomic-force multimode scanning probe microscope IIIa (AFM) (Digital Instruments Vecco Metrology Group, Santa Barbara, CA, USA). Furthermore, the PIM was characterized by scanning electron microscopy (SEM). The SEM image of the membranes was obtained with a Hitachi SU 3500 SEM/EDS (energy-dispersive spectroscopy) microscope operated at 10.0 kV (Hitachi, Tokyo, Japan).

2.1.3. Characterization of wastewaters

Three types of post-galvanic wastewaters were used in the studies - zinc, nickel, nickel-chromium; they were initially cleaned using the method of precipitation with milk of lime. Table 1 shows the physicochemical parameters and concentration of the metal ions in three types of wastewaters, which were used in the studies.

<table>
<thead>
<tr>
<th>Type of Wastewater</th>
<th>Zinc</th>
<th>Chromium</th>
<th>Nickel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (ppm)</td>
<td>25</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

According to the content of the regulation of the Minister of Environment [14] concentrations of metals in wastewater after the process of initial cleansing still exceeded the limit values. In zinc wastewater the amounts of zinc and chromium were, respectively, 30 and 8 times higher than the authorized concentration of those metals in wastewater released into the water and the ground. In nickel-chromium wastewater, concentrations of nickel, zinc, and chromium were, respectively, for nickel 2,2-, for zinc 12,6-, and for chromium 2,3-times higher than the authorized concentration [14]. An especially high exceedance of nickel content was observed in nickel wastewater. It was, approximately, 974 times higher than the authorized concentration of this metal in wastewater that can be released into the water or the ground [14].

2.2. Transport studies

Transport experiments were carried out in a permeation cell described in earlier papers [13]. The membrane film (surface area of 4.9 cm²) was tightly clamped between two cell compartments. Both the source phase and the receiving aqueous phase (45 cm³ each) were mechanically stirred at 600 rpm.

Fig. 1. Structure of the 3-propyl-pentane-2,4-dione.
Wastewaters were used in the source phase, whereas the receiving phase was a 0.5 M solution of sulphuric acid. The PIM transport experiments were carried out at 20°C ± 0.2°C. Small samples of the aqueous receiving phase were taken periodically from the sampling port equipped with a syringe and analyzed by atomic absorption spectroscopy (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA) to determine zinc(II), chromium(III) and nickel(II) concentrations. The source phase’s pH of 7.6 was kept constant using tetramethylammonium hydroxide.

2.3. Sorption process

Studies on Zn(II), Ni(II), Cr(III) ion sorption were conducted using the earlier-obtained sorbent in which 3-propyl-pentane-2,4-dione was the active substance.

To study the sorption process of heavy metals, 1 g +/- 0.0001 g of the obtained sorbent was weighed each time. For sorption testing, a 50 cm³ of galvanic wastewaters were used each time. The time of mixing investigated sorbent with solutions was 0.5, 1, 2, 4, and 8 h. The tests were performed at a temperature of 20°C and the atmospheric pressure.

Concentrations of metals in the solutions after a specified sorption time were analyzed by atomic absorption spectroscopy (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

The process of metal ion desorption was examined using 0.5 mol/L of H₂SO₄.

3. Results and discussion

3.1. Characterisation of the membrane

The surface of the studied membrane was characterized using AFM and SEM methods.

Fig. 2 shows the AFM image of the PIM. The membrane was visualized in a 10.0 × 10.0 µm image. On the image a slight roughness of the membrane is visible. The AFM method allows for estimating its value. The roughness (Rq) of the studied PIM was equal to 1.76 nm. Compared with other PVC-membranes, which we were studied in previous papers [15] this roughness is insignificant.

Fig. 3 presents, in turn, the SEM image of the tested membrane. The membrane was visualized in 100.0 × 100.0 µm image, so the magnification is ten times smaller compared with the AFM image. That is why on the SEM image only a dense and homogeneous structure is visible. The image confirms the results indicated by the AFM method concerning the roughness of the film surface. Carriers could crystallize in the membrane and their molecules migrated to the membrane surface, thus causing its roughness.

3.2. 3-propyl-pentane-2,4-dione as an active agent in PIMs and the sorbent

3-propyl-pentane-2,4-dione (Fig. 1) belongs to the group of β-diketones that exist in two tautomeric forms - ketone and enole (Eq. (1)).

\[
\begin{align*}
\text{C}_3\text{H}_3\text{O} - \\
\text{CH}_3\text{CH}_3\text{OH} \\
\text{C}_3\text{H}_7
\end{align*}
\]

Thanks to their interesting chemical structure (2 atoms of oxygen located closely in one plane) β-diketones from 6-membered chelate complexes of high durability with metal cations (Eq. (2)).

\[
\begin{align*}
\text{H}_3\text{C} - \text{O}^+ &\text{Cr}^{3+} &\text{H}_3\text{C} - \text{O}^-\\
\text{H}_3\text{C}_2\text{O} &\text{H}_3\text{C}_2\text{O} &\left(\text{C}_3\text{H}_7\right)_2
\end{align*}
\]
The capability of β-diketones to form durable complexes with many metal ions has been used in practice [16]. Compounds of this group are used as extractants in hydrometallurgy [17], as carriers in polymer membranes [18] and as sorbents [19].

3-propyl-pentane-2,4-dione was applied in this study (Fig. 1) as an active agent in polymer membranes as well as in sorption material.

3.3. Transport across PIMs

The results of the transport of metals across PIMs containing β-diketone as a carrier are depicted in Fig. 4 in the form of graphs of metal ion changes in the donor and the receiver phase in time.

Generally, as a consequence of metal ion transport across the membrane, the content of metal ions in the feed phase decreases, while it increases in the receiving phase.

As shown in Fig. 4, the concentration of metal ions in the feed phase decreases in the following order: Zn(II) > Cr(III) > Ni(II). Concentration of Zn(II) and Cr(III) ions in the feed phase decreases faster and finally reaches values lower than those of Ni(II). Concentration of Ni(II) ions in nickel and nickel-chromium waste before and after transport across PIMs remains constant.

Given the above fact, only a Zn/Cr separation coefficients were calculated using Eq. (3):

\[
S = \frac{C_{Zn(II)}}{C_{Cr(III)}}
\]  

where \(C_{Zn(II)}\) – concentration of Zn(II) ions (mg/L), \(C_{Cr(III)}\) – concentration of Cr(III) ions (mg/L).

\(S\) is equal to 1.23 and 1.17, respectively, for zinc and nickel-chromium wastewaters. As could be predicted the zinc(II) ions are separated with the highest efficiency from waste with lower conductivity.

The percentage of metal ion removal recovery factors (RF) from the solution was calculated using Eq. (4).

\[
RF = \left(\frac{C_i - C_f}{C_i}\right) \times 100\%
\]

where \(C_i\) is the initial concentration of metal ions in wastewater (mg/L), \(C_f\) is the concentration of metal ions in wastewater after time (mg/L).

Values of recovery coefficients (RF) of metals calculated from Eq. (4) for all types of the studied wastewaters are depicted in Fig. 5.

In the process of transport across PIMs with 3-propyl-pentane-2,4-dione as a carrier maximally 75%–78% of zinc and 62%–64% of chromium was recovered. Ni(II) ions are virtually not transported across this type of membrane. The percentage of zinc and chromium ions removal (RF) is almost on the same level in the case of zinc and nickel-chromium wastewater. The studied membrane process is suitable for additional cleansing of post-galvanic wastewaters of zinc and chromium ions that are present in them.

3.4. Sorption on PVC sorbent modified by β-diketone

3.4.1. Zinc-wastewaters

Table 2 presents the results of zinc and chromium sorption on 3-propyl-pentane-2,4-dione modified sorbent after a given time, and the amount of metal removed from the solution, calculated from formula (4).

As can be seen in Table 2, the lowest Zn concentration in zinc wastewater was obtained after 4 h-long sorptions, and it was equal to 0.112 mg/L which corresponds with 99.8% of zinc removal from the solution. On the other hand, the lowest concentration of Cr was obtained after an 8 h-long sorption, and it was equal to 0.063 mg/L which corresponds with 98.46% of chromium removal from the wastewater.

3.4.2. Nickel-wastewaters

Table 3 presents zinc and nickel concentrations in nickel wastewater after sorption on the studied sorbent, and the amount of metal that was removed from the solution.
As it can be seen in Table 3, the lowest zinc and nickel concentrations in nickel wastewater were obtained after an 8 h-long sorption, and they were equal to 0.01 mg/L for Zn(II) ions and 319.53 mg/L for Ni(II), which corresponds with 96.97% of zinc removal and merely 34.43% of nickel removal from the solution.

### 3.4.3. Nickel-chromium wastewaters

Table 4 presents zinc, nickel and chromium concentration after sorption on 3-propyl-pentane-2,4-dione modified sorbent and the amount of metal that was removed from the solution in that time.

In nickel-chromium wastewaters, the lowest concentration of Zn was obtained after an 8 h-long sorption. It was equal to 0.092 mg/L which corresponds with 99.6% of zinc removal from the solution. On the other hand, it was possible to obtain the lowest chromium concentration after a 4 h-long sorption, it was equal to 0.054 mg/L, which corresponds with 95.3% of chromium removal from the solution. In the following hours, its concentration increased marginally. In the case of nickel, the lowest concentration was obtained after 8-h-long sorption and was equal to 0.694 mg/L which constitutes approx. 37% of nickel removal from the solution.

As studies concerning sorption show the ions that adsorb best on 3-propyl-pentane-2,4-dione modified sorbent are zinc ions, their concentration in wastewater solutions after sorption was negligible. On the other hand, nickel ions were absorbed the worst; 34%–37% of them were removed from the solutions. This phenomenon is not entirely negative in this way the solution is enriched with Ni(II) ions.

Sorption capacity of PVC-β-diketone for Zn(II) and Cr(III) calculated from Eq. (5) was, respectively, 59.8 and 37.5 mg/g.

Table 2

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Concentration of Zn(II) ions in wastewater after sorption process (mg/L)</th>
<th>Concentration of Cr(III) ions in wastewater after sorption process (mg/L)</th>
<th>Removal of Zn(II) ions from wastewater after sorption process (%)</th>
<th>Removal of Cr(III) ions from wastewater after sorption process (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.820</td>
<td>0.842</td>
<td>95.28</td>
<td>79.36</td>
</tr>
<tr>
<td>1</td>
<td>1.910</td>
<td>0.723</td>
<td>96.81</td>
<td>82.28</td>
</tr>
<tr>
<td>2</td>
<td>0.620</td>
<td>0.453</td>
<td>98.96</td>
<td>88.90</td>
</tr>
<tr>
<td>4</td>
<td>0.112</td>
<td>0.192</td>
<td>99.81</td>
<td>95.29</td>
</tr>
<tr>
<td>8</td>
<td>0.114</td>
<td>0.063</td>
<td>99.81</td>
<td>98.46</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Concentration of Ni(II) ions in wastewater after sorption process (mg/L)</th>
<th>Concentration of Zn(II) ions in wastewater after sorption process (mg/L)</th>
<th>Removal of Ni(II) ions from wastewater after sorption process (%)</th>
<th>Removal of Zn(II) ions from wastewater after sorption process (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>425.5</td>
<td>0.030</td>
<td>12.69</td>
<td>90.91</td>
</tr>
<tr>
<td>1</td>
<td>400.36</td>
<td>0.028</td>
<td>17.84</td>
<td>91.52</td>
</tr>
<tr>
<td>2</td>
<td>384.15</td>
<td>0.014</td>
<td>21.17</td>
<td>95.76</td>
</tr>
<tr>
<td>4</td>
<td>367.21</td>
<td>0.012</td>
<td>24.65</td>
<td>96.36</td>
</tr>
<tr>
<td>8</td>
<td>319.54</td>
<td>0.010</td>
<td>34.43</td>
<td>96.97</td>
</tr>
</tbody>
</table>

In nickel-chromium wastewaters, the lowest concentration of Zn was obtained after an 8 h-long sorption. It was equal to 0.092 mg/L which corresponds with 99.6% of zinc removal from the solution. On the other hand, it was possible to obtain the lowest chromium concentration after a 4 h-long sorption, it was equal to 0.054 mg/L, which corresponds with 95.3% of chromium removal from the solution. In the following hours, its concentration increased marginally. In the case of nickel, the lowest concentration was obtained after 8-h-long sorption and was equal to 0.694 mg/L which constitutes approx. 37% of nickel removal from the solution.

As studies concerning sorption show the ions that adsorb best on 3-propyl-pentane-2,4-dione modified sorbent are zinc ions, their concentration in wastewater solutions after sorption was negligible. On the other hand, nickel ions were absorbed the worst; 34%–37% of them were removed from the solutions. This phenomenon is not entirely negative in this way the solution is enriched with Ni(II) ions.

Sorption capacity of PVC-β-diketone for Zn(II) and Cr(III) calculated from Eq. (5) was, respectively, 59.8 and 37.5 mg/g.

where \( q_t = \frac{(C_0 - C) \times V}{m} \)

Zn/Cr and Zn/Ni separation coefficients calculated from formula (3) are equal to 1.61 and 0.13, respectively.
3.5. Desorption

Regeneration of polymer sorption material was conducted using sulfur acid(IV) in accordance with the below reactions.

In the case of Zn(II) and Ni(II) ions reaction of desorption goes according to Eq. (6), in case of Cr(III) ion according to Eq. (7).

After washing the sorbent with sulfur acid three times, almost the entire amount of the adsorbed metal ions (approx. 99.8%) was moved into the solution.

3.6. Comparison of the effectiveness of wastewater thorough cleansing processes resulting from transport across membranes and in the process of sorption

Comparison of the effectiveness of recovering metals contained in wastewater using the method applied in the studies, namely as a result of transport across PIMs and in the process of sorption, is presented in Table 5. Thus, the possibility of conducting thorough cleansing of wastewater with the use of these methods was compared.

4. Conclusions

• Both in the process of transport across PIMs and the process of sorption the ions that are most effectively removed from post-galvanic wastewater are Zn(II) and Cr(III) ions.

• Using the membrane techniques 75%–78% of zinc and 62%–64% of chromium may be recovered, while in the sorption process it may be 97%–99% of zinc and 95%–98% of chromium. Sorption on 3-propyl-pentane-2,4-dione

Table 4
Concentration of zinc(II), nickel(II) and chromium(III) ions in nickel-chromium wastewaters after sorption on PVC-3-propyl-pentane-2,4-dione sorbent and amount of metal ions removed from the nickel-chromium wastewaters

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Concentration of Ni(II) ions in wastewater after sorption process (mg/L)</th>
<th>Concentration of Cr(III) ions in wastewater after sorption process (mg/L)</th>
<th>Concentration of Zn(II) ions in wastewater after sorption process (mg/L)</th>
<th>Removal of Ni(II) ions from wastewater after sorption process (%)</th>
<th>Removal of Cr(III) ions from wastewater after sorption process (%)</th>
<th>Removal of Zn(II) ions from wastewater after sorption process (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.987</td>
<td>0.670</td>
<td>1.260</td>
<td>10.27</td>
<td>42.24</td>
<td>94.99</td>
</tr>
<tr>
<td>1</td>
<td>0.923</td>
<td>0.430</td>
<td>1.080</td>
<td>16.09</td>
<td>62.93</td>
<td>95.70</td>
</tr>
<tr>
<td>2</td>
<td>0.862</td>
<td>0.112</td>
<td>0.463</td>
<td>21.64</td>
<td>90.34</td>
<td>98.16</td>
</tr>
<tr>
<td>4</td>
<td>0.775</td>
<td>0.054</td>
<td>0.212</td>
<td>29.55</td>
<td>95.34</td>
<td>99.16</td>
</tr>
<tr>
<td>8</td>
<td>0.694</td>
<td>0.057</td>
<td>0.092</td>
<td>36.91</td>
<td>95.09</td>
<td>99.63</td>
</tr>
</tbody>
</table>

Table 5
Comparison of the effectiveness of transport across PIMs and the sorption process in metal recovery from post-galvanic wastewater

<table>
<thead>
<tr>
<th>PIMs</th>
<th>Sorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(II) and Cr(III) ions are transported best</td>
<td>Zn(II) and Cr(III) ions are adsorbed best</td>
</tr>
<tr>
<td>75%–78% of zinc and 62%–64% of chromium can be recovered</td>
<td>97%–99% of zinc and 95%–98% of chromium can be recovered</td>
</tr>
<tr>
<td>Effective results were obtained after 8 h of duration of the process</td>
<td>Effective results were obtained after 2–4 h of duration of the process</td>
</tr>
<tr>
<td>Ni(II) ions remain in wastewater. The maximum amount of removed nickel ions is approx. 4.5%</td>
<td>Approx. 37% of nickel ions can be recovered</td>
</tr>
<tr>
<td>Zn/Cr separation coefficients are equal to 1.23 and 1.17, respectively, for zinc and nickel-chromium wastewater</td>
<td>Sorption capacity of the studied composite for Zn(II) and Cr(III) was 59.8 and 37.5 mg/g, respectively</td>
</tr>
<tr>
<td>It requires frequent replacement of membranes</td>
<td>Zn/Cr and Zn/Ni separation coefficients are equal to 1.61 and 1.13, respectively, for zinc and nickel-chromium wastewater</td>
</tr>
<tr>
<td>Possible regeneration of sorption material</td>
<td></td>
</tr>
</tbody>
</table>
modified sorbent is a more effective method of heavy metal ion separation from post-galvanic wastewater.

- Somewhat higher Zn/Cr separation coefficients are obtained in the process of sorption than in membrane transport.

- Both methods are not effective for Ni(II) ion removal as wastewater that contains ions of this metal exceeds its authorized concentration in wastewater solutions, and cannot be released into the water or the ground directly. During sorption, Ni(II) ions are broken down between eluent - wastewater solution, and in the membrane process, they virtually remain in wastewater. Ni(II) ions should be removed using another method, for example electrolytically.

- Due to economic reasons, sorption on PVC-β-diketone granules is a more advantageous method in thorough cleansing of post-galvanic wastewater. The sorbent can be effectively regenerated and used several times.

Acknowledgments

The new developments presented in this paper were carried out within the 2007–2013 Innovative Economy Operational Programme, Sub-action 1.3.2., Support of the protection of industrial property generated by scientific entities as a result of R&D works within project no. UDA-POIG.01.03.02-04-077/12-01, financed by the European Regional Development Fund (ERDF) (85% of co-financing).

In order to finance project no. UDA-POIG.01.03.02-04-077/12-01, the authors received a direct subsidy amounting to 15% of co-financing. A part of the project costs were covered by the Kujawsko-Pomorskie Regional Operational Programme (9% of co-financing).

The authors would like to express their gratitude to the Kujawsko-Pomorskie Regional Operational Programme for financial support, and to the European Union for co-financing this project.

In order to protect intellectual property generated as a result of R&D works, the authors applied for a patent under the title "NP-1: Method for removal of metal ions from wastewater" (Polecam, Patent Application No. POIG.01.03.02-04-077/12-01), which is currently under examination. The development presented in this paper was authorized by the Ministry of the Environment in Case of Substances Particularly Harmful to the Aqua Environment (Act of 18 November 2004, Journal of Laws, No. 152, item 1291).

Symbols and abbreviations

- AAS — Atomic absorption spectroscopy
- AFM — Atomic-force microscopy
- b LOQ — Beyond the limit of quantification
- C — Concentration of metal ions in wastewater after time, mg/L
- \( C_{\text{Cr(III)}} \) — Concentration of Cr(III) ions, mg/L
- \( C_i \) — Initial concentration of metal ions in wastewater, mg/L
- COD — Chemical oxygen demand
- CPs — Chelating polymers
- CTA — Cellulose triacetate
- \( C_{\text{Zn(II)}} \) — Concentration of Zn(II) ions, mg/L
- DAO — Di(2-ethylhexyl) adipate
- EDS — Energy dispersive spectroscopy
- m — Mass of the sorbent, g
- PIM/PIMs — Polymer inclusion membrane/polymer inclusion membranes
- PVC — Polyvinyl chloride
- \( q_i \) — Sorption capacity, mg/g
- RF — Percentage of metal ion removal
- Rq — Roughness
- S — Separation coefficient
- SEM — Scanning electron microscopy
- THF — Tetrahydrofuran
- V — Volume of the solution, L

References


[14] Regulation of the Minister of the Environment in Case of Conditions Which Should be Done when Entering Sewage into Waters or into the Ground, and in Case of Substances Particularly Harmful to the Aqua Environment, November 18, 2014.


