Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20588

91 (2017) 146–151
October

Assessing the removal of heavy metals in industrial wastewater by means of chemical exergy

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Received 27 December 2016; Accepted 12 February 2017

ABSTRACT

Industrial processes may frequently produce wastewater with high concentrations of heavy metal ions. Heavy metals can be harmful both for the environment and for the human health even in small concentrations. This study has the scope to assess the efficiency of four different sorbent-assisted ultrafiltration methods that were applied for enhancing the treatment of industrial wastewater. Each treatment has different levels of removal success for each heavy metal ion. In the framework of this manuscript chemical exergy is utilized as an evaluating parameter of mass fluxes. The total efficiency of each treatment method is assessed by calculating the total chemical exergy dissipation of each mass flux. All the treatment methods successfully removed more than 96% of copper and lead ions while the performances with respect to nickel and zinc ions removal were more erratic. The ultrafiltration/bentonite absorption had the best overall performance with a total chemical exergy dissipation of 66.82%, and ultrafiltration/vermiculite absorption had the second best overall performance with 64.29%. The method was able to combine different parameters and return meaningful results that can be used for optimization of wastewater plants treatment management.

Keywords: Ultrafiltration; Absorption; Exergy dissipation; Zeolite; Bentonite

1. Introduction

The development of mining, metal-plating and fertilizer production industries is correlated with the increased concentrations of non-biodegradable contaminants in the discharged effluents, especially heavy metals [1]. Although their chemical and physical properties may vary significantly, in principle heavy metals have a greater specific gravity than 5 and atomic weights from 63.5 to 200.6 Da [2]. The inherent characteristics of heavy metals are such that even in low concentrations may have a significant polluting effect. In addition, according to the Environmental Protection Agency [3], the high solubility of heavy metals increases the hazard of being absorbed by living organisms and causes health disorders. Fu and Wang [1] pointed out that wastewater effluents from chemical-intensive industries are highly contaminated with heavy metal ions of nickel, copper, zinc and lead that have high toxic and carcinogenic potential and notable environmental impact. Thus, controlling the concentration of heavy metals in the effluent water from wastewater treatment plants is of high interest not only for industrial wastewater facilities but also for municipal wastewater [4].

Kurniawan et al. [5] presented a review of the treatment methods for effluents with inorganic loads, like heavy metals,

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Presented at the 13th IWA Specialized Conference on Small Water and Wastewater Systems & 5th IWA Specialized Conference on Resources-Oriented Sanitation, 14–16 September, 2016, Athens, Greece.

and identified seven primary methods that are: chemical precipitation, coagulation–flocculation, dissolved air flotation, ion exchange, ultrafiltration, nanofiltration and reverse osmosis. The technology readiness level varies between these technologies since some of them are available for commercial applications, and others are only tested on lab or pilot scales. But what is derived from this study [5] is that the application of a single treatment method cannot be totally effective for the whole range of heavy metals. On one hand, there are widely applied and relatively inexpensive treatments like chemical precipitation and absorption. On the other hand, membrane filtration systems have high efficiencies but can be very costly. Barakat [6] reviewed 94 recent studies regarding treatment methods of heavy metals in wastewater and concluded that the methods that receive the most attention are membrane filtration and absorption. The most representative membrane filtration treatment is identified to be ultrafiltration. On the other side of the scale, new absorbents with improved properties have raised the attention on absorption treatments.

Ultrafiltration is one of the common membrane filtration technologies, with the others being nanofiltration [7], reverse osmosis [8] and electrodialysis [9]. It works in relatively low transmembrane pressures and uses a permeable membrane to separate the compounds of interest. Nonetheless, ultrafiltration membranes have porous sizes that in principle are larger than the dissolved heavy metal ions in wastewater. As a result, ultrafiltration membranes have been combined with surfactants, and novel techniques have been developed for improving the removal efficiency. The most common method that can be found in the recent literature is micellar-enhanced ultrafiltration [10]. In some cases biosurfacants were used, like rhamnolipids, which are a class of glycolipids that are produced by the rod-shaped bacterium *Pseudomonas aeruginosa*. Thus, the rejection ratio of wastewaters from metallurgical industries was increased even up to 99% [11]. An alternative pathway to improve ultrafiltration has been the utilization of polymers that are water-soluble and, for the purpose of removing heavy metals, metal-binding. This method is known as polymer-enhanced ultrafiltration, which by binding the heavy metal ions into more complex molecules enhances the ability of the porous to filter out the compounds of interest [12]. Finally, the utilization of ceramic membranes, a method known as ceramic membrane ultrafiltration, may prolong significantly the operational life of the system while providing chemical and thermal stability [13]. Although ultrafiltration can be very efficient when the described enhancements are applied, it still remains a very expensive method [14].

Absorption methods can be a very effective treatment solution for the removal and the recovery of heavy metals. In addition, the integration of low-cost absorbents like zeolites and bentonite can successfully replace activated carbon and reduce the cost of operation [15]. Moreover, these materials have high specific surface areas and are prevalent in most soils [16]. Zeolites have an outstanding ion-exchange capacity and have the ability to remove heavy metal cations from wastewater [17]. Recent advances in waste management have made possible the reuse of fly ash from coal combustion for developing zeolites and extending the life cycle of materials [18]. Bentonite is a silicate clay mineral with very low permeability and high specific area [19]. In particular, sodium bentonites have improved features in comparison with raw bentonite like cation-exchange capacity and thermal stability. Therefore, they are more suitable for the removal of heavy metal cations [20]. Vermiculite is a hydrated magnesium aluminum silicate mineral and has a structure that allows high cation-exchange capacity [21]. Gharin Nashtifan et al. [22] showed that vermiculate is able to absorb simultaneously and efficiently nickel and copper cations. Nonetheless, absorption has drawbacks in respect to universal applicability since it is highly dependent on the pH of wastewater and the ionic strength. A combination of absorption and ultrafiltration could enhance the efficiency of removal and recovery process of heavy metals in industrial wastewaters while limiting the overall treatment costs.

Most of the wastewater treatment studies focus on the reduction of the concentrations of compounds after treatment but very few attempts to assess the mass fluxes and assigning them characteristic values that would be representative of the overall quality of the effluent. The exceptions are represented by works that use life-cycle assessment (LCA) to assess the wastewater treatment plants performance [23]. However, LCA has been implemented through different methodologies. The ILCD Handbook [24] names 11 different methodologies and provides suggestions for the selection of the most suitable method for each case. Nonetheless, selecting the correct methodology remains a subjective task and may be a cause of bias. In addition, the variety of software tools and their corresponding databases introduce further variability in the final outputs of the analysis. Finally, the presentation of the environmental impacts with incomparable indicators may provide results that can be confusing and of scarce utility.

Therefore, this study aims to utilize chemical exergy as an objective thermodynamic parameter for evaluation of heavy metal mass fluxes in industrial and municipal wastewater. It should be pointed out that chemical exergy will be here applied exclusively for the assessment of the mass fluxes. Hybrid methodologies that combine exergy and LCA, although very popular [25], are not considered since they are affected by the previously described LCA limitations.

The present work utilizes the experimental results from Katsou et al. [26] where ultrafiltration and absorption were combined in order to optimize the removal of heavy metals from industrial wastewater streams. Ultrafiltration was enhanced by incorporating several absorption methods, and the full description of the experiments and the analysis will be presented in the section 2 "Materials and methods". Some of these methods have been proved to be effective to some extent. Nonetheless, the degree of effectiveness can only be quantified on an individual basis for each heavy metal substance. There is a lack of evaluation methods of mass fluxes in terms of quality assessment. The present study introduces a method that utilizes the chemical exergy of heavy metal substances and their respective concentrations in order to assess qualitatively the mass fluxes and the efficiency of heavy metal removal. In addition, an integrated method has been developed that returns one single efficiency value of the removal process for all the heavy metal substances that are contained in a flow. The scope is the development of a management and optimization tool for wastewater treatment plants that takes into consideration the total exergy dissipation of a group of substances in the different treatment processes within a wastewater treatment plant.

2. Materials and methods

This section is separated into two parts. The former provides information gathered from a previous research work and explains how the results are used in the present work. The latter deals with the concept of chemical exergy and the development of an integrated assessment method for the mass flows of heavy metal cations.

2.1. Experimental parameters and utilized results

The experiments that are presented in this subsection have been conducted by Katsou et al. [26], and the results will be here used as input for the calculation of chemical exergies of the flows. The heavy metal cations of interest were Pb(II), Cu(II), Zn(II) and Ni(II). The initial concentration of these cations was regulated at 320 mg/L by dissolving nitrate salts in the wastewater and by dilution when necessary.

Four different configurations were utilized for treating industrial wastewater with high concentrations of heavy metal cations. Initially the industrial wastewater was treated solely by means of ultrafiltration. At a second stage ultrafiltration was assisted by coupling absorbents with the ultrafiltration membrane. Bentonite, zeolite and vermiculite were utilized in their natural form and without undergoing any chemical processing. The experiments were performed by agitating the solutions at 800 rpm for 2 h at pH = 6. The concentration of the heavy metal cations in the effluent wastewater are shown in Table 1.

2.2. The concept of chemical exergy and development of a methodology

In principle, exergy represents the maximum amount of energy of a system that has the ability to be converted in other forms of energy, especially work [27]. This work can be obtained by driving the system into a reversible equilibrium with its natural environment. There are several different types of exergy but the two primary are physical and chemical exergies. On one hand, physical exergy is the reversible work of a system that comes into thermal and mechanical equilibrium with its surrounding environment and is directly correlated with the temperature and the pressure difference between the system and the surrounding environment. In this case the physical exergy represents the difference of the system and its environmental reference state. On the other hand, chemical exergy is correlated to the chemical structure and the chemical bonds of a substance. Assuming a system is at its environmental reference state, i.e., in the same temperature and pressure with the surrounding environment, chemical exergy represents the maximum attainable energy of this system when it comes into chemical equilibrium with the surrounding environment and thus transitions from the environmental reference state to the dead-end state when the system is in mechanical, thermal and chemical equilibrium with its environment. The chemical exergy of species is defined in accordance with their presence in the standard reference environment. For the case of gases that exist in the standard atmosphere, e.g., nitrogen, their chemical exergy is calculated by assessing the work that would be performed by their isothermal expansion in a turbine. For the species that do not exist in the standard reference environment, then the chemical exergy calculation is a two-step process. First, the compound of interest reacts under standard temperature and pressure with species that naturally exist in the standard atmosphere for the production of substances that naturally exist in the reference environment. Then, the concentrations of products and reactants are changed from the standard conditions to the state that they are in equilibrium in the standard reference environment and vice versa [28]. The standard chemical exergy of nickel, zinc, copper and lead cations can be found in Table 2.

Chemical exergy has been used in the past to analyze natural resources in smaller but also bigger scale. Chen [30] calculated the "overall exergy budget consumption of the earth" in order to highlight the issues concerning global sustainability. Huang et al. [31] used exergy as a unified method for assessing the quality of water resources and introduced a comprehensive index of organic pollution analysis that utilized established parameters like BOD_5. Similarly, Chen and Ji [32] introduced the specific relative chemical exergy indicator for the assessment of the water quality and showed that this indicator is "a practical indicator for anthropogenic water exploitation". Finally, chemical exergy has been also used as a tool for assessing the organic matter in water flow [33].

Nonetheless, exergy should not be confused with Gibbs free energy although their definitions appear to be similar. Gibbs free energy is the available enthalpy of an isobaric and isothermal process, and is independent of the conditions of the systems surroundings. Exergy is a wider term that describes the maximum attainable work of a system that reversibly comes to equilibrium with its surroundings; therefore, exergy is dependent on the systems surroundings. Also in real life applications most processes do not propagate

Table 1
Concentration of nickel, zinc, copper and lead in permeate resulting by the combined mineral-UF system at pH = 6 [26]

Treatment	Ni(II) (mg/L)	Zn(II) (mg/L)	Cu(II) (mg/L)	Pb(II) (mg/L)
UF	246	220	13.1	2.61
Bentonite–UF	194	138	7.2	0.12
Zeolite–UF	230	203	8.4	0.70
Vermiculite–UF	170	165	10.10	1.39

Note: Process: the mineral addition is performed into wastewater in a one-stage process.

Table 2
Chemical parameters of nickel, zinc, copper and lead [29]

Substance	Molecular mass (kg/kmol)	Enthalpy of devaluation (kJ/mol)	Standard chemical exergy (kJ/mol)
Ni(II)	58.71	239.74	232.7
Zn(II)	65.37	419.27	339.2
Cu(II)	63.54	201.59	134.2
Pb(II)	207.2	305.64	232.8

reversibly, and these "irreversibilities" reduce the amount of maximum attainable work by a value that is usually defined as energy.

The method of analysis of this study focuses on the calculation of the chemical exergy of inlet and outlet heavy metal cations not only individually for every compound but also collectively for all the compounds combined. The basic calculation approach can be found in Eq. (1):

$$b_{ch}\ \text{eff}\ (\%) = \sum mi \times b_{ch}i(\text{out}) / \sum mi \times b_{ch}i(\text{in}) \qquad (1)$$

with b_{ch} eff (%) standing for chemical exergy efficiency, *mi* for the corresponding mass, $b_{ch}i$(in) for the chemical exergy of the input and $b_{ch}i$(out) for the chemical exergy of the output. The principle approach behind this method is that the successful removal of the heavy metal cations is reflected by the dissipation of their chemical exergy. The scope is to assess the combined dissipation of chemical exergy for all the heavy metal cations in all the different types of treatment and return a single efficiency value that reflects the overall performance. The calculation of the chemical exergy dissipation is shown in Eq. (2):

$$b_{ch}\ \text{dis}\ (\%) = 1 - b_{ch}\ \text{eff}\ (\%) \qquad (2)$$

with b_{ch} dis (%) representing the percentage of chemical exergy dissipation.

3. Results and discussion

The analysis of chemical exergy has been done on the basis of 1 L of wastewater. Fig. 1 shows the chemical exergy of Ni(II) for the different treatment scenarios. The input is at the level of 1.4 KJ, and all the treatment methods reduce the Ni(II) chemical exergy below 1 KJ for every liter of output.

As we observe in Fig. 1, the combination of vermiculite–absorption/ultrafiltration results to the highest reduction levels of Ni(II) chemical exergy, and the combination of bentonite–absorption/ultrafiltration is a close second. In relation to the absolute amount of kilojoules, Zn(II) chemical exergy had the highest value among all the examined heavy metal cations. The results are shown in Fig. 2. For this heavy metal ion, the combination of bentonite–absorption/ultrafiltration performed best with the combination of vermiculite–absorption/ultrafiltration being the second best alternative.

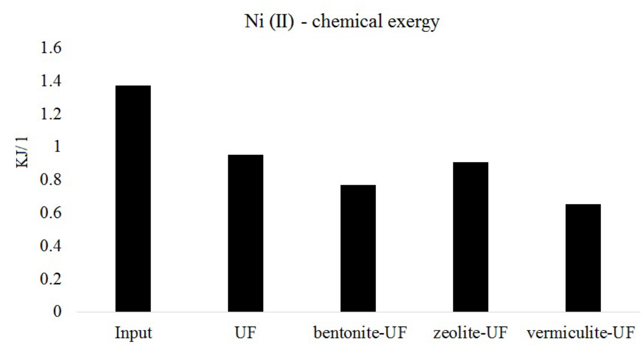

Fig. 1. Chemical exergy (in KJ/L) of Ni(II) for 1 L of input and treated wastewater.

The chemical exergy of Cu(II) was reduced tenfold, and Pb(II) chemical exergy was reduced hundredfold for all the treatments. Thus, a graphical representation of these results would not be useful. Therefore, these values are shown in Table 3. For both cases the combination of bentonite–absorption/ultrafiltration performs better than the other treatments, although all of them seem to perform well. Contrary to the cases of Ni(II) and Zn(II), the combination of vermiculite–absorption/ultrafiltration performed worse than the other absorption/ultrafiltration combinations. It should be denoted that the application of vermiculite absorption does not improve significantly the operation of ultrafiltration for the case of Pb(II) and Cu(II) in comparison with ultrafiltration being applied solely. This is an interesting result that could assist the unnecessary integration of vermiculite absorption if the scope is the removal of Cu(II) and Pb(II).

As mentioned in the section 2 "Materials and methods", the scope of this manuscript is to use the dissipation of the exergies as an efficiency indicator of each treatment. For this purpose, Eq. (2) is applied for each different heavy metal ion and for the four different treatment scenarios. The results are shown in Table 4.

The highest dissipations are observed for lead and copper cations. Especially for the case of lead the dissipation reaches 100% for the case of bentonite/ultrafiltration treatment. Contrary to that, the dissipation of Cu(II) exergy is higher for all the combinations of absorption/ultrafiltration in comparison with ultrafiltration. But what comes out as a general observation for Table 4 is that each treatment may have better selectivity and better performance for different types of heavy metal cations. For example, zinc cations are optimally

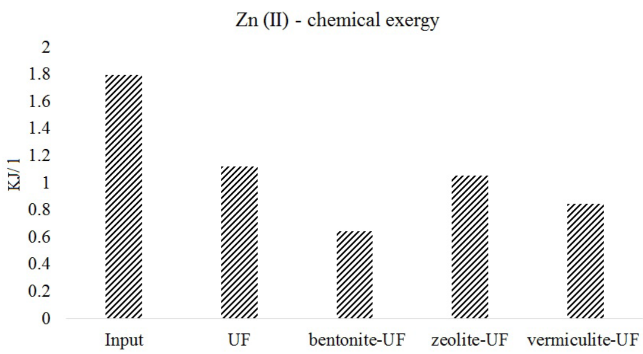

Fig. 2. Chemical exergy (in KJ) of Zn(II) for 1 L of input and treated wastewater.

Table 3
Chemical exergy (in J) of Cu(II) and Pb(II) for 1 L of input and treated wastewater

	Cu(II)	Pb(II)
Input	739	393.1
UF	26	2.79
Bentonite–UF	15	0.13
Zeolite–UF	17	7.84
Vermiculite–UF	21	1.55

Table 4
Chemical exergy dissipation of the heavy metal cations for the different types of treatment

Treatment	Ni(II)	Zn(II)	Cu(II)	Pb(II)
UF (%)	30.5	37.7	96.4	99.3
Bentonite–UF (%)	44.1	64.2	97.9	100.0
Zeolite–UF (%)	33.9	41.5	97.6	98.0
Vermiculite–UF (%)	52.5	52.8	97.1	96.0

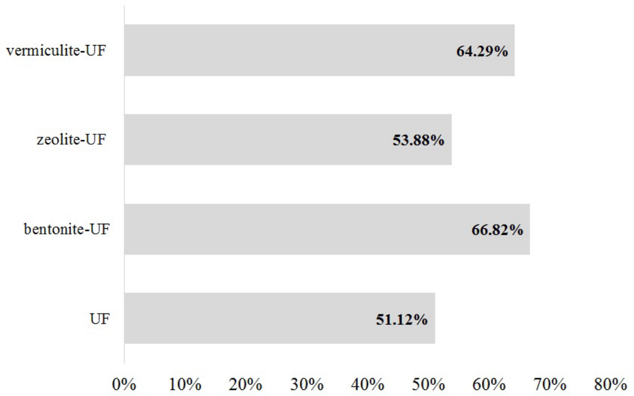

Fig. 3. Percentage of total chemical exergy dissipation of the four treatments.

removed by the combination of ultrafiltration/bentonite absorption, but nickel cations are optimally removed by the combination of ultrafiltration/vermiculite absorption.

Therefore, in Fig. 3 the total chemical exergy dissipation is calculated for each different treatment process. The combination of ultrafiltration/bentonite absorption has the overall better performance, and the non-assisted ultrafiltration has the worst performance relatively to the other treatments.

An interesting outcome of the analysis is that the total chemical exergy dissipation of the non-assisted ultrafiltration has only slightly worse overall performance than the combination of ultrafiltration/zeolite absorption, and this should be taken into consideration when choosing if it is beneficial to combine absorption with ultrafiltration in respect to cost and overall improvement. In general, this methodology is able to return a single value that can be characteristic of a treatment method in respect to a specific set of compounds.

An initial interpretation of this analysis method may not reveal a straightforward connection between the dissipation percentages of heavy metal cations concentrations and the assessment of their reduction below the limits set by legislation. However, in the cases of industrial wastewater treatment, the compositions tend to be relatively constant, and a minimum chemical dissipation percentage can be assigned to each compound of interest.

In the field of wastewater treatment, exergy has only been used to assess the energy efficiency of the wastewater treatment plants and to reflect the overall energy balance, i.e., energy supply and energy production, especially for the cases that biogas is produced by means of anaerobic digestion of sludge. There are studies where the total exergy of a wastewater plant is analyzed [34,35]. In this cases physical exergy balance vastly outweighs chemical exergy, especially of metals, and the results focus more on the energetic efficiency of the processes than the removal of compounds. Metallurgical industry is one of the few sectors where destruction of exergy is used as a management tool [36], but again the integration of physical exergy shifts the focus from the materials and diverts it to the efficiency from an energy perspective.

A future application of this suggested methodology is the assessment of biofilm processes like moving bed biofilm reactors and trickling filters. Free-floating microorganisms conglomerate into polymers, commonly known as biofilm, which can be physically separated from the wastewater stream. The chemical exergy of the produced biofilm can be calculated by means of elemental analysis and calculation of the relevant chemical exergy factor. The level of chemical exergy dissipation of the wastewater directly relates to the removal efficiency of pollutants.

4. Conclusions

This study introduced a methodology for assessing the removal of heavy metal cations in industrial wastewater by means of chemical exergy dissipation. These methodologies were non-assisted ultrafiltration and sorbent-assisted ultrafiltration with bentonite, zeolite and vermiculite respectively. On one hand, each different compound has different rates of reduction for each treatment. On the other hand, a treatment may be more successful for the removal of a specific compound and less successful with the removal of another. Chemical exergy is an objective method to assign numerical values, representative of the thermodynamic quality, to mass fluxes of heavy metals. The methodology returned the total dissipation of the mass fluxes for the four types of treatment. The combination of ultrafiltration/bentonite absorption had the overall best performance. Future applications of this methodology may include the performance analysis of biofilm processes by assessing the chemical exergy of the produced biomass.

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