REMOVAL OF HEAVY METALS FROM WASTEWATER USING CAUSTIC CALCINED MAGNESIA

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Abstract

Slovakia holds 4th to 5th position in the world with respect to the supplies and mining output of magnesite. The most important product of natural magnesite processing is magnesia. While dead-burnt magnesia is used for producing basic refractory materials for metallurgy and cement industry, caustic calcined magnesia (CCM) founds new applications in industries, agriculture and environment protection. Use of CCM, due to its alkaline nature, as a reactive material for remediation of wastewaters, can provide all advantages of methods based on neutralization (pH adjustment) by lime. In this study, CCM was experimentally tested as a reactive material for the removal of cations Cu^{2+}, Zn^{2+} and Ni^{2+} from wastewaters. The effects of chemical composition of model wastewaters tested and water-to-CCM weight ratio were investigated. The results have shown that CCM is a suitable material for the removal of heavy metals, especially copper, zinc and nickel, from acid wastewaters. The efficiency of cation removal up to 100% has been observed.

1 Introduction

Industrial activities give rise to large quantities of wastewater containing toxic heavy metals [1]. At the present time, industrial wastewater represents a serious environmental problem, not only for its ever-increasing quantity, but also for great diversity [2]. There is a broad variety of industrial wastewater based on different industries and combinations of contaminants [3]. Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries [3, 4]. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. This results in serious environmental problems in the environment and caused negative effects to the eco-systems and human life´s [3]. Like the various characteristics of industrial wastewater, the treatment of industrial wastewater must be designed specifically for the particular type of effluent produced. The conventional methods for removing heavy metals from wastewater include different processes such as chemical precipitation, ion exchange, solvent extraction, adsorption, or membrane filtration [3, 5, 6]. Chemical precipitation is the most widely used process in industry because it is relatively simple and inexpensive to operate [2, 6]. Metals can be removed by precipitation as insoluble metal hydroxides, sulfides, carbonates, and phosphates [4, 7]. Typically, the metal precipitated from the solution is in the form of hydroxide according to Eq. (1). [3, 4, 6, 7]

$$M^{2+} + 2\,(OH^-) \quad \longleftrightarrow \quad M(OH)_2 \downarrow \qquad\qquad (1.)$$
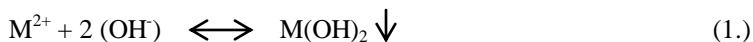
where M^{2+} and OH^- represents the dissolved metal ions and the precipitant and $M(OH)_2$ is an insoluble metal hydroxide [3, 4,]. The solubility of many metal hydroxides in relation to the pH is given in Fig. 1. It can be seen that the minimal solubility of the hydroxides of the majority of metals can be extracted from this diagram [7, 8].
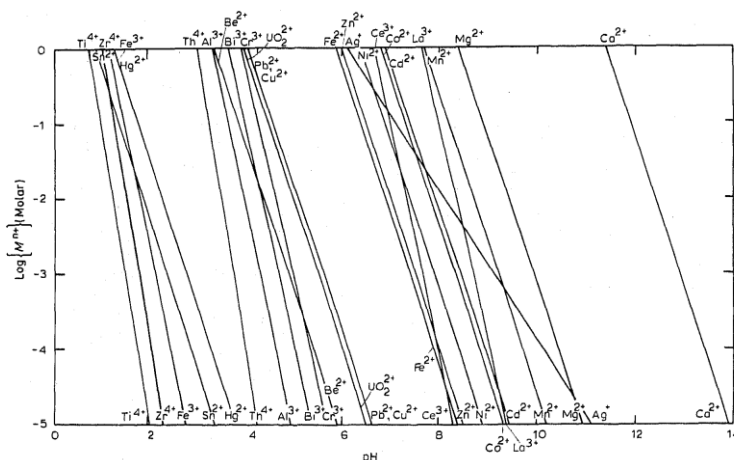

Fig. 1   Precipitation diagram of hydroxides at the 25 °C [8]

Lime, limestone and caustic soda (NaOH) are the most commonly employed precipitant agents due to their availability and low-cost in most countries [3, 9]. As an alternative to lime and caustic soda, the use of caustic calcined magnesia (CCM) to precipitate heavy metals from wastewater has been employed in recent years [10, 11]. CCM (MgO) is used in environmental control technology and compared to most commonly used alkalis (CaO, $Ca(OH)_2$, NaOH, $NaHCO_3$) it presents essential advantages [10]. In aquatic environment MgO transforms into $Mg(OH)_2$ following the reaction (2) [12]:

$$MgO + H_2O \longrightarrow Mg(OH)_2 \qquad\qquad (2.)$$

Theoretically, the pH of a saturated $Mg(OH)_2$ slurry is about 10, but in reality, given the presence of other ions, buffer solutions can be formed with pH of 9-9,5 [12-15]. Due to the milder basic character and low solubility of $Mg(OH)_2$, CCM as a reactive material in passive remediation systems is very useful due to its relatively low environmental impact, and the safety of its transportation and use, as well [16, 17].

Magnesite ($MgCO_3$) is the most important raw material, which occurs in Slovakia in sufficient quantity and acceptable quality. CCM can be produced by calcination (thermal decomposition) of magnesite, following the reaction (3) [18]:

$$MgCO_3 \longrightarrow MgO + CO_2 \qquad\qquad (3.)$$

The aim of this study was to test the CCM prepared from Slovak magnesite as a potential reactive material for removal of heavy metals from acidic industrial wastewaters. Different values of S:L ratios were used and the efficiency of heavy metals removal from acid wastewater was measured.

2   Experimental material(s) and methods

Reactive material

Bulk magnesite concentrate (1 – 10 mm) supplied by the company SMZ Jelšava was used in the present study. Prior to the batch tests, fraction <1 mm was prepared by homogenization and sieving. Thereafter, the magnesite was milled in a vibration mill and calcined at temperature 640 °C and dwell time of 180 minutes in an electric muffle furnace. For the batch experiments, the sample of CCM with grain size ranging from 80 to 250 µm was obtained by dry-sieving. The contents of the main elements were determined by the AAS method and the specific surface area of CCM was determined by the BET method. The physico-chemical properties of the caustic calcined magnesia samples are shown in **Table 1**.

Table 1 Physico-chemical properties of the CCM sample used

Chemical composition [wt. %]						Specific surface area $[m^2 g^{-1}]$
SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Loss on Ignition	
0.4	6.1	0.4	8.8	82.3	1.2	51

Wastewaters

First of all, two model wastewaters were prepared to find an optimum S:L (CCM : wastewater) ratio - the first one with high content of iron (referred to as DB) and the second one practically without iron (DBB). These model wastewaters were prepared by dissolving chemicals - the sulphates of $Fe^{2+/3+}$, Mn^{2+}, Zn^{2+}, Al^{3+}, Cu^{2+}, Ni^{2+} in distilled water. Concentrations of individual metals in synthetic wastewaters determined by inductively coupled plasma (ICP) method are shown in **Table 2**.

Table 2 Chemical composition of model wastewaters

Model wastewater sample	pH	concentrations of metals [mg/l]						
		Fe	Mn	Cu	Zn	Ni	Al	As
DB	3.24	1118.5	14.75	**22.54**	**24.67**	**0.75**	7.21	0.04
DBB	3.49	0.41	16.18	**25.35**	**30.13**	**3.29**	0.098	0.169

To investigate the efficiency of heavy metals removal from wastewaters using CCM, two samples of real wastewaters (D HPV, D C11) from an industrial area in Bratislava were used. The pH and electrical conductivity of the wastewaters were measured immediately after sample collection. Samples for chemical analysis were acidified using concentrated nitric acid (HNO_3) and analysed by ICP method. The concentrations of heavy metals in real wastewaters are shown in **Table 3**.

Table 3 Chemical composition of real wastewaters

Real wastewater sample	pH	concentrations of metals [mg/l]						
		Fe	Mn	Cu	Zn	Ni	Al	As
D HPV	2.1	1369	11.65	**28.79**	**15.89**	**0.335**	170	6.711
D C11	5.6	23.11	34.76	**0.366**	**7.772**	**0.223**	0.413	0

Laboratory batch tests

In each test, a defined amount (0.8, 0.4 or 0.2 g) of CCM was added to 40 ml of synthetic or real wastewater in a glass tube. The tubes were mechanically mixed at room temperature for 2 hours. Then the slurries were filtered, pH of the filtrates was measured, the filtrates were acidified using concentrated HNO_3 to decrease the pH and stabilize the solution prior to chemical analysis, and finally analysed by ICP method. The efficiency (E) of the heavy metals removal from was calculated using Eq. 4

$$E = \frac{c_0 - c_r}{c_0}.100 \qquad (4.)$$

where: c_0 - the initial concentration [mg/ L] and c_r is the final concentration [mg/ L] of Cu^{2+}, Ni^{2+} and Zn^{2+}.

3   Results and discussion

In this study, the effect of the S:L ratio (1:200, 1:100, 1:50) and the pH on the efficiency of the removal of the selected heavy metals (Cu, Zn, Ni) from the wastewaters used. Precipitation diagram in Fig.1 illustrates that the pH range 8 -10 seems to be optimal to precipitate the copper, zinc and nickel from an aqueous solution. It can be assumed, that - as the pH is increased - the copper (pH 7.5 - 8) is precipitated as the first, followed by zinc (pH 8 - 9) and nickel (pH 9 - 10). The results of preliminary experiments carried out with model wastewaters showed that the final pH values were in the range 9 to 10 for all the CCM:DBB ratios used. In case of wastewater DB the situation was different: final pH values of 10.0, 9.5 and 4.7 were obtained for the S: L ratio = 1:50, 1:100 and 1:200, respectively. The final pH value of 4.7 measured at S:L=1:200 is far from the optimal pH value for any of the monitored heavy metals. It can be assumed, that the decrease in pH was due to a higher content of iron in DB and preferential precipitation of $Fe(OH)_3$, and only a residual part of the reactive material (CCM) was used to remove Cu^{2+}, Ni^{2+} and Zn^{2+}, according to the precipitation diagram in **Fig. 1**. Thus, the pH which is needed to remove zinc and nickel need not have been reached. This hypothesis was confirmed by the values of residual concentrations of Cu^{2+}, Ni^{2+} and Zn^{2+} after precipitation. In case of the wastewater DBB, the efficiency of copper, zinc and nickel removal had not been affected by the value of S:L ratio, and all the three monitored heavy metals were completely removed. On the other hand, only copper could be removed from the wastewater DB at the S:L ratio 1:200, 1:100 and 1:50, while zinc was completely removed at the S: L ratio = 1: 50 and S: L = 1: 100, and the efficiency of only about 65% was observed at the S:L ratio = 1:200. Nickel was completely removed at the S: L ratio = 1: 50, but at the S:L ratio = 1:100, the efficiency was decreased to 70%, and at the S:L ratio = 1:200 practically no nickel was removed. Hence, S:L ratio of 1:100 and 1:50 had been chosen for the tests with the real wastewaters.

The values of the efficiency of heavy metal removal, calculated using Eq. (4) are compared for both samples of real wastewater in **Fig. 2** (sample D HPV) and **Fig. 3** (sample D C11). All the three monitored heavy metals were practically completely removed from the wastewater D HPV at the S:L ratio 1:50 and 1:100 – see **Fig. 2**. Slightly lower efficiencies (97 to 100 %) for all monitored metals was observed in case of the wastewater D C11 (**Fig. 3**).
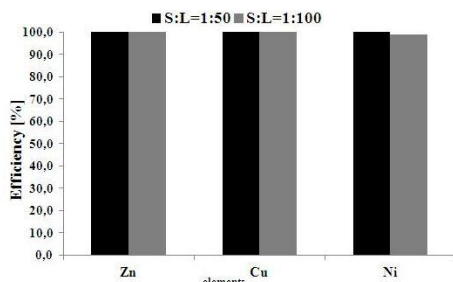
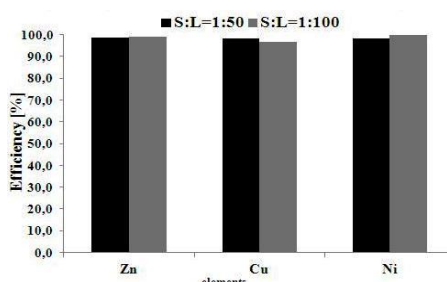**Fig. 1** Efficiency of Zn^{2+}, Cu^{2+}, Ni^{2+} removal from wastewater D HPV

Fig. 2 Efficiency of Zn^{2+}, Cu^{2+}, Ni^{2+} removal from wastewater D C11

Comparison of the final pH values measured in the real wastewaters after the precipitation of hydroxides, as shown in **Figs. 4** and **5**, allows for a more detailed explanation of the observed results, discussed above. The final pH values in both samples of real wastewater were practically identical, in pH range 9 and 10. Only in case of HPV, the final value of pH was 8.69 at the S:L ratio 1:100, but no effect on the effective removal of monitored metals has been observed. The high pH is likely to be caused by a high content of reactive MgO due to the optimal thermal treatment of raw magnesite tested.
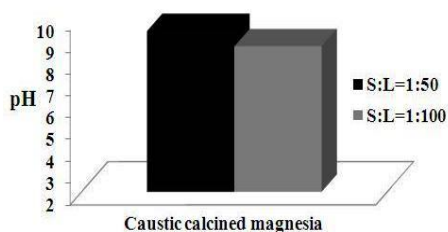

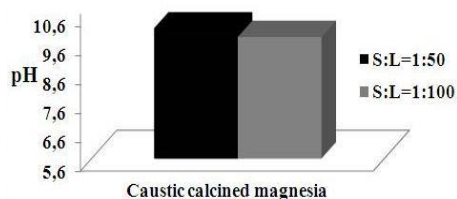**Fig. 3** Comparison pH for two ratios added CCM in D HPV

Fig. 4 Comparison pH for two ratios added CCM in D C11

4 Conclusion

In this study, caustic calcined magnesia (CCM) was tested as a potential reactive material for the removal of Cu^{2+}, Ni^{2+} and Zn^{2+} from industrial wastewaters. The effect of the pH and S:L (CCM:wastewater) ratio on the efficiency of copper, zinc, and nickel removal from model and real wastewaters was investigated. Based on the present results, it can be concluded that:

- CCM prepared and tested in the present study was characterised by a high content of reactive MgO due to the optimal calcination temperature and time used.
- The S:L ratio did not affect the efficiency of Cu^{2+} removal.
- The S:L ratio 1:200 was insufficient to remove Zn^{2+} and Ni^{2+} from model wastewater.
- All the three monitored heavy metals were completely removed from real industrial wastewaters at the S: L ratio = 1:50 and 1:100. The final pH values were practically identical in all tests, in pH range 9 and 10, representing nearly optimal pH for precipitation of corresponding insoluble hydroxides.

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