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Treatment of industrial slag zinc ferrite by zeolitic sludge

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Abstract. The study reports the results in the removal efficiency of the metals released by zinc ferrite in aqueous systems, using a zeolitic sludge as an ion exchanger. The so-called zinc ferrite is an industrial waste produced during the treatment of minerals for zinc extraction. The zeolitic sludge used in the experimental campaign is a by-product that derives from industrial processes and contains a combination of synthetic zeolites such as 4A (LTA) and 13X zeolite (FAU). Initially, different systems have been prepared, with predefined weight ratios of zeolitic sludge/zinc ferrite/water. The systems were analyzed, at different times, by plasma mass spectrometry (ICP-MS) that allowed to measure the variation of concentration of Fe, Mg, Ca, Zn, Mn, Pb, Na, K ions. Zeolitic sludges were efficient for the total absorption of Pb and Zn ions.

1. Introduction

The protection of the environment is a current problem. There are several threats that put human health and the entire ecosystem at serious risk and with particular repercussions on the quality of air [1-3], water [4, 5] and soil [6]. The growing sensitivity towards these problems is orienting the research to find new solutions in all the sectors, as the preparation and use of eco-sustainable materials [7-14], new chemical eco-friendly process [15-21] but also towards materials that can be advantageously used for the degradation of pollutants [22-27]. Industrial wastes represent, in many cases, a serious danger to the environment because they can contain metals that can be released over time into water or into soil [28, 29].

Generally, materials capable of removing pollutants by adsorption or ion exchange are used to reduce the level of the released pollutants, and among these zeolites and zeotopes [30-39] can be listed. Zinc ferrite, the subject of this research campaign, is an industrial slag that is produced by the extraction of zinc from minerals. In particular, the zinc ferrite used in this work is from an industrial plant located in southern Italy. It contains a multiplicity of elements [40]. Recent studies have reported that metals released by zinc ferrite in aqueous systems can be removed using ion exchangers such as ETS-10 [41], an effective ion exchanger and adsorbent material [42-48] that belongs to the Engelhard titanium silicate family [49-54]. In this work authors investigate the use of a zeolitic sludge, a by-products of industrial processes that contains a combination of synthetic zeolites, for the removal of metals released by zinc ferrite in aqueous systems.



2. Materials and methods

2.1. Materials

Zinc ferrite contains many heavy elements among which the most abundant are Fe, Zn, Pb, Ca, Mn, Al, Mg, Cu, Na, K, etc., that can be released by the zinc ferrite in aqueous environment [41]. It appears as a brown powder (Figure 1). XRD analysis of Zeolite sludges (Figure 2a) was carried out on a Rigaku MiniFlex 600 X-ray diffractometer with CuK (wavelength of 1.5406 Å). Radiation was generated at 20 mA and 40 KV. Powdered samples have been scanned with 0.02° 2θ step at a rate of 1°/minute and showed the presence of 4A (LTA) and the 13X (Faujasite) zeolites, calcium, sodium and potassium carbonates as crystalline phases. The zeolitic sludge appears as a white powder (Figure 2b). The morphology of the powder has been examined on a scanning electron microscope (FEI model INSPECT) (Figure 2c). It is characterized by the presence of agglomerates mainly containing Al, Si and Na as obtained by EDS analysis, thus confirming XRD findings (Figure 2d).



Figure 1. Zinc Ferrite.

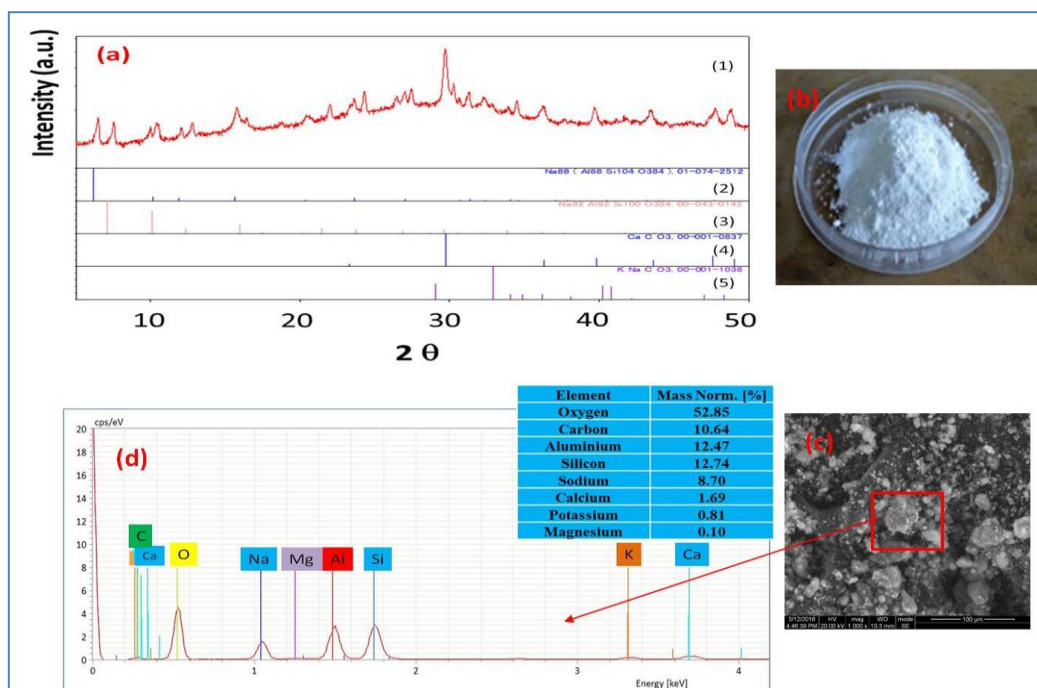


Figure 2. Zeolitic sludge characterization: (a) XRD diffractograms: (1) zeolitic sludge, (2) 13X zeolite, (3) 4A zeolite, (4) Calcium carbonate, (5) Sodium-Potassium carbonate; (b) Powdered zeolitic sludge; (c) Particles morphology by SEM; (d) Elemental composition as obtained by Energy-dispersive X-ray spectroscopy.

2.2. Characterization

The instrument used to determine the concentrations of the elements was a Plasma mass spectrometry (ICP-MS). It was performed using an ICP-MS Perkin-Elmer Elan DRC instrument. For this analysis, some elements were monitored as Fe, Mg, Ca, Zn, Mn, Pb, Na, K.

The experimental conditions were: plasma power 1100 W, gas flow rate in the nebulizer 0.75 mL/min, quartz nebulizer, CeO/Ce oxide ratio <3%, sample flow 1 mL/min, argon refrigerant flow speed 15 L/m, dwell time 50 ms, scan mode Peak hopping, sweeps/reading 40, reading/replicate 1, and 3 replicates.

2.3. Preparation of aqueous systems

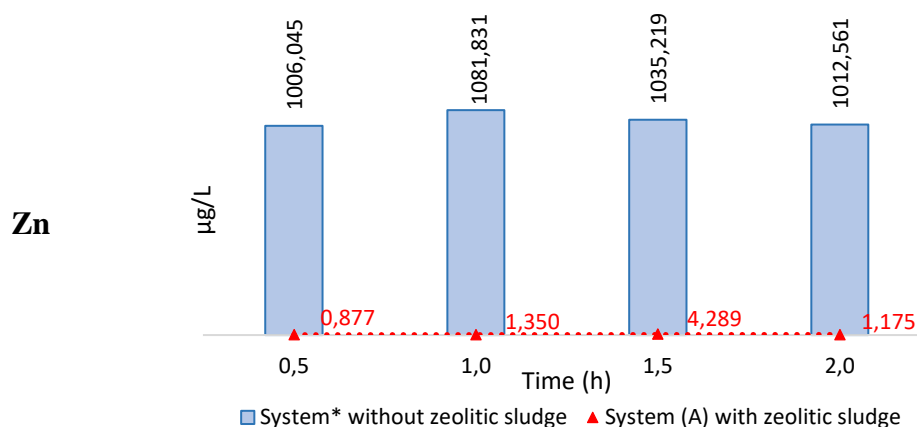
The system was prepared by mixing 5 g of ferrite and 10 g di zeolitic sludge in 100 mL of distilled water and stirring at room temperature for the following times: 0.5, 1.0, 1.5, and 2.0 hours (Table 1). The zeolitic sludge was immersed into the systems in a closed sachet of filter paper in order to facilitate its final recovery. At the end of the pre-established contact time, each bag containing zeolitic sludge was removed and the system was filtered. The obtained solution was subjected to ICP-MS analysis.

Table 1. Prepared system for the treatment of metal removal from zinc ferrite.

Composition system A
10 g zeolitic sludge + 5 g Zinc Ferrite + 100 mL H ₂ O
with stirring times: 0.5, 1.0, 1.5, 2.0 hours

3. Results and discussions

The concentration of the elements in solution after treatment with zeolitic sludge at different stirring times are shown below. These data have been compared with the concentrations referred to the system already reported in previous articles [41], characterized by the same composition but in the absence of zeolitic sludge (5g Zinc Ferrite / 100 mL H₂O). Figure 3 shows the graphs relating only to the elements that have been positively removed from the zeolitic sludge, such as Zn, Pb, Mn, Ca and Mg. It is possible to observe that the abatement of these elements is very important, and presents a constant trend over time for Zn and Pb while for Mn, Ca and Mg a slight decrease is evident over time.



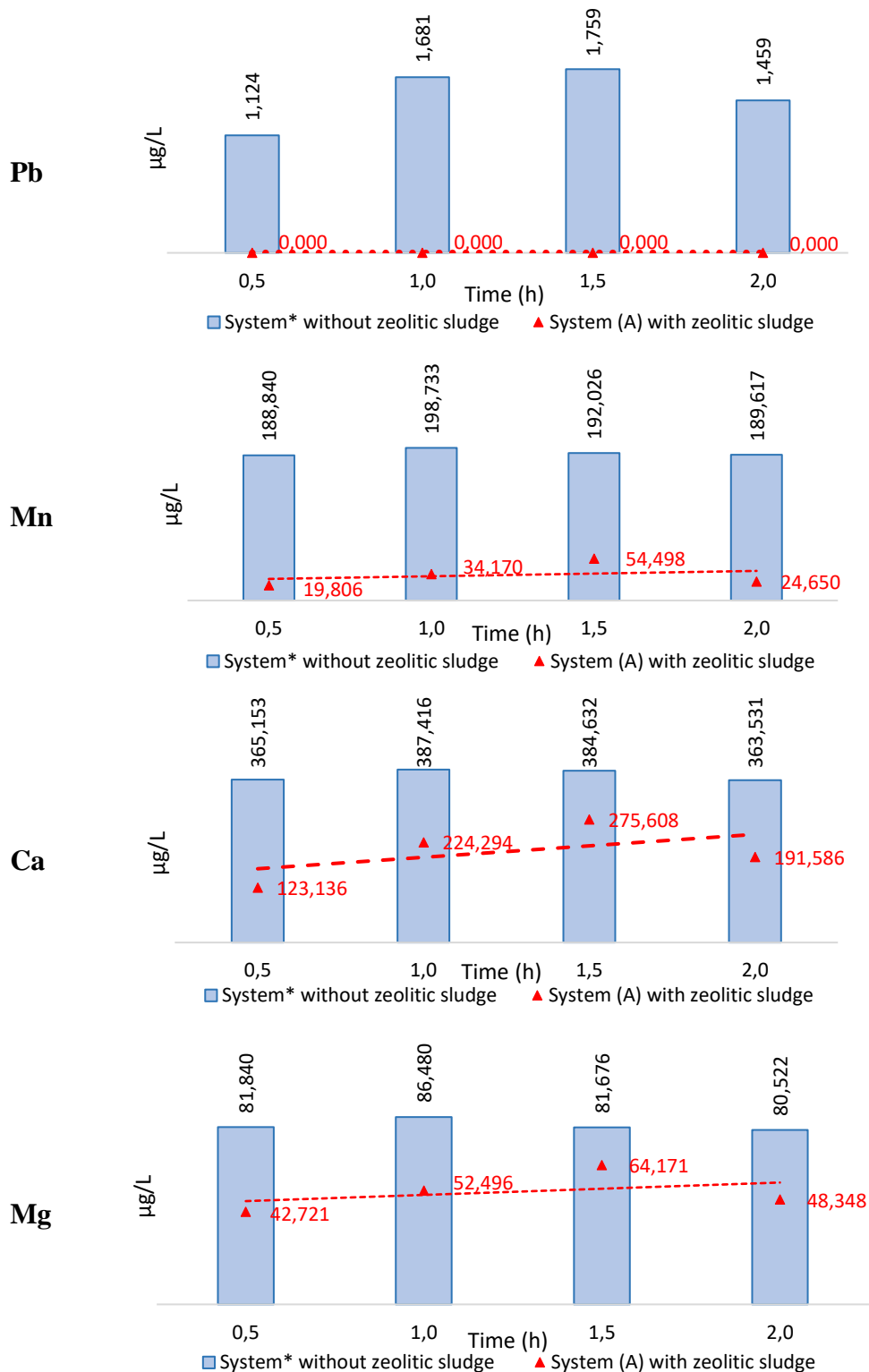


Figure 3. Concentrations of the elements Zn, Pb, Mn, Ca and Mg in the system A (zeolitic sludge / Zinc Ferrite / H₂O) as a function of the stirring time and comparison with the data relating to the system* in the absence of zeolitic sludge (Zinc Ferrite / H₂O) reported in previous articles [41].

Observing the data in Table 2 which shows the percentage of abatement, it is possible to observe how the Pb is completely removed, followed by the zinc which shows an almost total abatement.

Table 2. Percentage abatement (%) for the elements Pb, Zn, Mn, Ca, Mg, in system A, as a function of the stirring time.

Element	Stirring time (h)			
	0.5	1.0	1.5	2.0
Pb	100.00	100.00	100.00	100.00
Zn	99.91	99.88	99.59	99.88
Mn	89.51	82.81	71.62	87
Ca	62.28	42.11	28.35	47.30
Mg	47.80	39.30	21.34	39.96

The abatement of the studied elements by zeolitic sludge therefore follows the following order Pb> Zn> Mn> Ca> Mg. Furthermore, it can be seen that for the stirring time of 1.5 hours there is a common decrease in the abatement percentages, with the exception of the Pb. This phenomenon can be justified by considering the complex system of zinc ferrite within which different equilibrium and dissolution reactions develop over time. An hour and a half can be considered as the stirring time in which the peak of solubilization phenomena of the zinc ferrite components is reached. All this creates a more complex and more competitive system. The subsequent increase in the percentage of abatement to two hours is the consequence of the recovery of adsorption phenomena by zeolitic sludge.

Iron deserves a separate discussion. From the following Figure 4 which shows a graph, similar to the previous ones but related to iron, it appears that the iron is completely removed in the first half hour, but over time it is restored to the system reaching a complete release in solution at an hour and a half and a partial recovery to two hours.

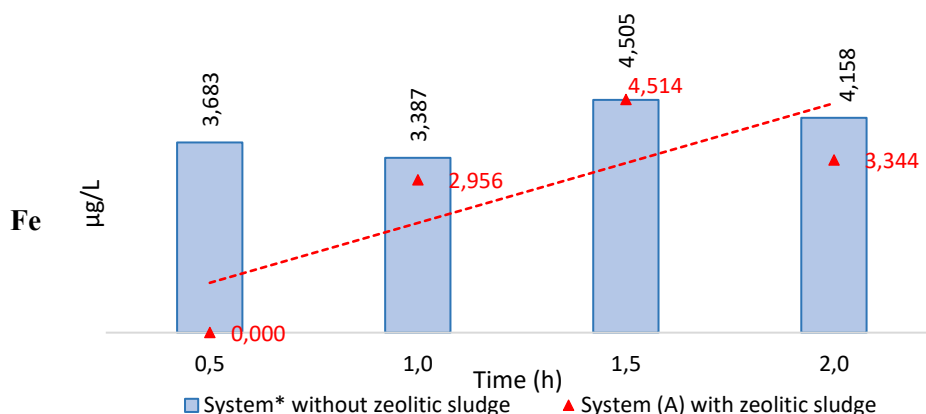


Figure 4. Concentration of Fe in system A (zeolitic sludge / Zinc Ferrite / H₂O) as a function of the stirring time and comparison with the data relating to the system* in the absence of zeolitic sludge (Zinc Ferrite / H₂O) reported in previous articles [41].

From the data reported in Table 3 where the percentage of iron abatement is reported as a function of the stirring time, it is possible to observe that for a time of half hour there is a 100% percentage reduction. However, the abatement percentage reaches its criticality at an hour and a half where a value of 0.00% is obtained. Also in this case it is confirmed that there are strong dissolution reactions of other elements of the zinc ferrite which are competitive with iron and which lead again to the

release of iron in solution. After an hour and a half there is a partial recovery of equilibrium and iron adsorption reactions, but which nevertheless presents a moderate reduction of about 20%.

Table 3. Percentage abatement (%) for Fe, in system A, as a function of the stirring time.

Element	Stirring time (h)			
	0.5	1.0	1.5	2.0
Fe	100.00	12.73	0.00	19.58

The following Figure 5 shows the trend of the elements that did not show a reduction but rather an increase in their concentrations. These elements were Na and K.

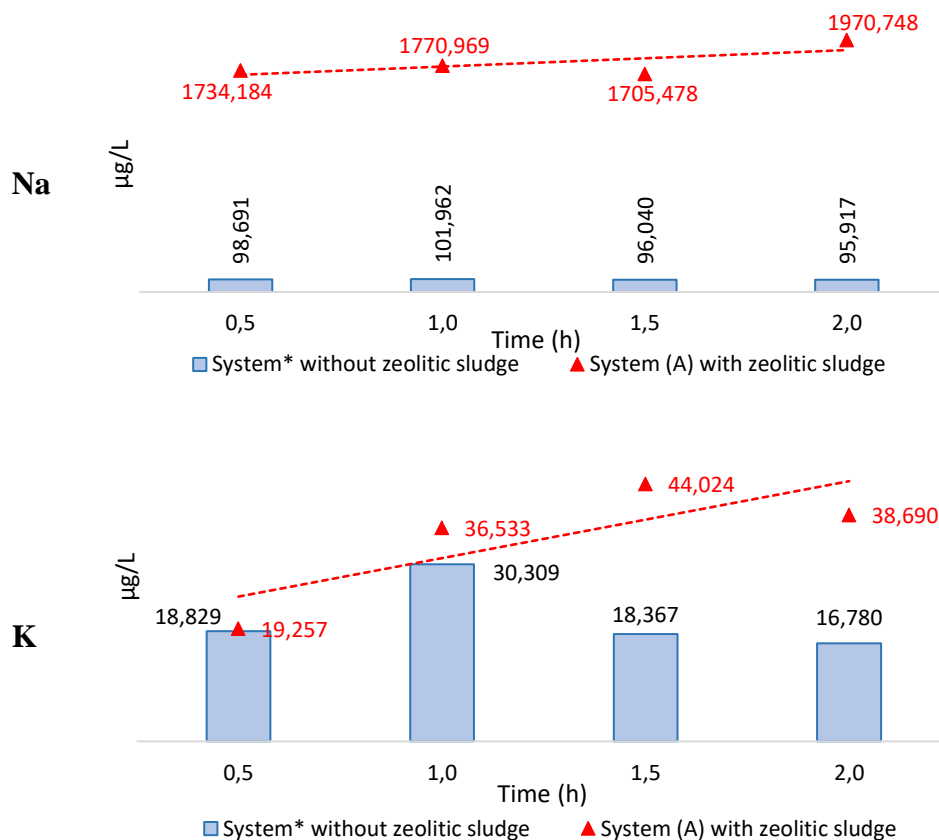


Figure 5. Concentrations of the elements Na and K in the system A (zeolitic sludge / Zinc Ferrite / H₂O) as a function of the stirring time and comparison with the data relating to the system* in the absence of zeolitic sludge (Zinc Ferrite / H₂O) reported in previous articles [41].

Table 4. Percentage abatement (%) for the Na and K, in system A, as a function of the stirring time.

Element	Stirring time (h)			
	0.5	1.0	1.5	2.0
Na	+ 1657.59	+1636.89	+1675.80	+1954.64
K	- 2.27	+20.54	+139.69	+130.57

In particular, Table 4 shows the percentage variation of the concentrations of the Na and K. The data shows that the Na concentrations increase significantly even for short times. This is justified by the high sodic nature of the zeolites which constitute the zeolitic sludge and which demonstrates their exchange action. As far as the concentration of K is concerned, it undergoes a very slight reduction to 0.5 hours and then reaches an increase in concentration.

All this can be justified, also in this case, with the potassic nature of the zeolites present in the zeolitic sludge, which although it has a lower potassium component than the sodium one, lead to having a release of potassium over time as a testimony to the exchange.

4. Conclusions

The zeolitic sludge, used for the removal of some elements released by the zinc ferrite in water, is highly efficient for the removal of Zn and Pb. In fact, already after half an hour their abatement was almost total: 100% for the Pb and 99.91% for the Zinc. A slightly lower, but still important, efficiency was recorded for the Mn, Ca and Mg which reported a reduction of 89.51%, 62.28% and 47.80% respectively.

The stirring time of an hour and a half was critical as there was a tendency to decrease the abatement percentages. This is due to the fact that for this time there have been more dissolution reactions of the components of the zinc ferrite which have established competition phenomena between the different elements that have gone into solution.

The use of zeolitic sludge has instead led to an increase in solution of the concentrations of Na and K demonstrating the exchange that has taken place.

The use of zeolitic sludge has proved to be double-advantageous, both because it allows an efficient removal of some elements released by the zinc ferrite in water and because it is possible to restore a new use to an industrial sub-product.

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