Removal of pharmaceutical contaminants by hydrotalcite-like compounds synthesized from aluminum saline slag wastes

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Introduction

The aim of this study is to find an adsorbent capable of retaining emerging pollutants, namely pharmaceutical compounds, from water. These chemical compounds are not usually monitored in water bodies but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects.

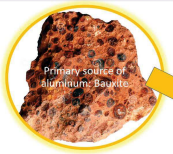
diclofenac

Salicylic acid

Aluminum source and adsorbent synthesis

The recycling of aluminum is an esencial part of its industry. It has a much lower environmental impact than its extraction from bauxite.

Once the aluminum is used it can be very effectively recycled and in this recycling process salt fluxes are used as they have multiple functions: they disperse mechanically the oxides and metals, and they isolate the metal from the atmosphere. This addition of the salt fluxes to the process produces saline slag which is the main waste of the secondary aluminum process



Saline slag is classified as hazardous waste thus is storaged in controlled landfills

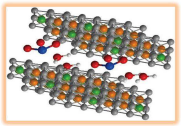
Alternative: recovery of the aluminum present in the saline slag

Dry residue, its aluminum was extracted and used for the synthesis of the adsorbents

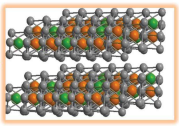
Synthesis of layered double hydroxides (LDH) also known as hydrotalcite-like compounds

LDH were synthesized by the co-precipitation method with a molar ratio Me^{2+}/Al^{3+} of 3:1. Four samples were synthesized using cobalt, magnesium, nickel and zinc as Me^{2+}.

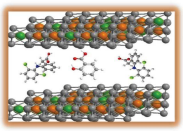
Alkaline extraction procedure:
Slags with a 2 mol/dm³ NaOH solution for 1 hour



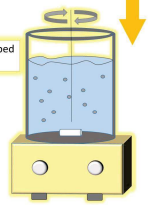
Samples were calcined for 4 h at 673 K to extract the water and anions of the interlayer and form mixed metal oxides (MMO).



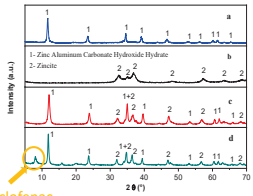
The MMO were then employed in the adsorption of emerging contaminants



Both diclofenac and salicylic acid were succesfully adsorbed in the interlayer of the LDH due to its memory effect



Characterization and adsorption results



Diclofenac

Figure 1. Powder X-ray diffraction patterns of non-calcined (a) calcined (b), rehydrated (c) and rehydrated with diclofenac (d) Zn sample.

LDH	Theoretical oxides structure	Theoretical remaining mass (%)	Measured remaining mass (%)	Variance from theoretical value
$Co_6Al_2CO_3(OH)_{16}\cdot 4H_2O$	$2Co_3O_4+Al_2O_3$	71.89	69.30	-2.59
$Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$	$6MgO+Al_2O_3$	56.92	54.30	-2.62
$Ni_6Al_2CO_3(OH)_{16}\cdot 4H_2O$	$6NiO+Al_2O_3$	67.89	64.17	-3.72
$Zn_6Al_2CO_3(OH)_{16}\cdot 4H_2O$	$6ZnO+Al_2O_3$	69.40	69.06	-0.34

Table 1. Comparison of theoretical remaining mass and measured remaining mass of the LDH samples.

- The thermal analysis behavior observed mass losses compared to those expected theoretically
- Zn_6Al_2 had the best correlation between theoretical and empirical results

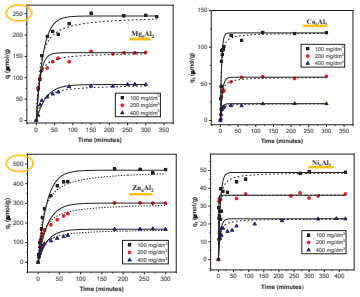
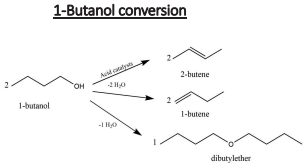


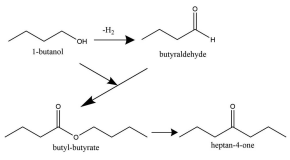
Figure 2. Comparison of the kinetic data (diclofenac adsorption capacity) of the different samples

- The effect of the adsorbent dose was examined by changing the amount of adsorbent in solutions with a fixed initial drug concentration
- Kinetic modelling: in this study pseudo-first- (solid line) and pseudo-second-order rate equations (dotted line) were applied to test the experimental data
- Magnesium and zinc LDH have greater adsorption results
- Co_6Al_2 and Ni_6Al_2 are not capable of recovering its previous hydrotalcite configuration
- The equilibrium is also achieved faster in Co_6Al_2 and Ni_6Al_2

1-Butanol conversion



Scheme 1. 1-butanol dehydration pathways.



Scheme 2. 1-butanol dehydrogenation pathways.

- The 1-butanol conversion was used as a means of acidity and basicity characterization of the MMO
- Results were compared with the adsorption performance of the samples
- A relationship between the amount of pollutants adsorbed and the butenes formed in the dehydration reaction of 1-butanol was found.

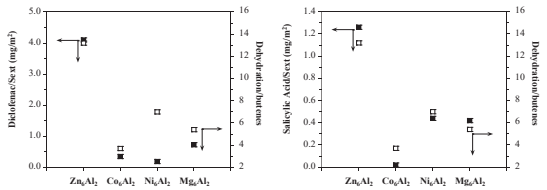


Figure 3. Evolution of the amount of pollutants adsorbed/Sext to the butenes formation in the dehydrogenation reaction of 1-butanol. (■) pollutants (□) dehydration

Conclusions

A series of LDH with various Me^{2+} and a ratio of 3:1 was synthesized using Al^{3+} extracted from saline slags as aluminum source. All the samples have a LDH structure with differences between samples mainly due to Me^{2+} cations. Adsorption experiments of diclofenac and salicylic acid as examples of emerging contaminants were performed. Zn_6Al_2 and Mg_6Al_2 present the best adsorption capacity mainly due to their ability to recover their LDH structure when rehydrated. The adsorption capacities of the adsorbents correspond quite well to their acidic properties. Not so much in the case of the basic properties because the dehydrogenating capacity of the LDH samples is also affected by the redox properties of metals, Ni and Co.

Acknowledgements

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