



Adsorption of Chromium (VI) by metal hydroxide sludge from the metal finishing

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Abstract: Metal finishing industries produce an important tonnage of metal hydroxide sludge (MHS) during the treatment of their liquid effluents charged with heavy metals. Generally, a small part of these sludge is valorized because of their important metal fickleness. Consequently, the majority of these metal hydroxide sludge is sent to landfill centers. We propose to valorize this sludge by using them as pollutant sorbent in order to retain the polluting species contained in the industrial aqueous effluents. The chosen pollutant for this preliminary study is Chromium (+VI). Starting from an experimental well defined protocol, various parameters have been studied (chemical nature of the sludge, solid/liquid ratio, concentration of the pollutant, particle size) in order to determine the experimental parameters which influence the sorption yield of these sludge and thus to validate the feasibility of an industrial application of this new way of valorisation. First results point out that the sorption yield is more than 95% independently from the experimental conditions. Moreover, experiments highlight that the sludge mass (and so sorbent sites) is THE only real parameter which influences the yield. In this article, a review of the patents on different aspects of the valorisation of polymetallic hydroxide sludge as pollutant trappers is presented.

Keywords: valorisation, sorption, polymetallic hydroxide sludge, Cr^{VI}

1 Introduction

Industrial aqueous pollution (heavy metals) accounts for 30 to 40% of industrial pollution. Metal finishing is one of the sectors which contributes mostly to this pollution. Due to its unique production, metal finishing consumes and discharges wastewater containing metallic ions, cyanide, COD, etc.. Therefore, this activity is bound to the European Integrated Pollution Prevention and Control Directive since 1996, known as the "IPPC Directive" [1]. In France, this directive is translated "as is" for metal finishing workshops through the ministerial order of June 30th, 2006. Before 1996, this text was already part of the legislation of the officially identified sites for the protection of the environment codification 2565 [2]. This ministerial order defines thresholds in terms of pollutants in the effluents and in terms of flow yield and concentration of specific chemical species for this branch of activity. These workshops must implement curative or preventive Best Available Techniques (BAT) which is another major principle of the IPPC Directive [3]. For about 65% of workshops, initiatives and actions designed to limit environmental impacts are typically curative. Concerning wastewater composed mainly of heavy metals, the detoxication process of wastewater is the co-precipitation of metal ions in hydroxide. Some species such as chromates may require an oxidation/reduction treatment. After filtration, hydroxides obtained as sludge are disposed of in various sectors. This sequence of processes is described in the BAT reference documents (BREF), on "Best Available Techniques for metal finishing treatment and plastic finishing treatment" [4]. It is important to take into account that France produces 180 000 tons of metal sludge per year compared to the overall European production which averages to 950 000 tons per year (source CETIM). Currently, despite the existence of processes such as hydrometallurgy for sludge rich in zinc, pyrometallurgy for sludge rich in nickel, thermal reconditioning for sludge with specific characteristics or finally added to cement for sludge rich in aluminium or iron, polymetallic hydroxide sludge (predominance of non-metal) are mostly eliminated in hazardous waste landfills. For these reasons, this research project's aim is to propose a new method of polymetallic hydroxide sludge valorisation that can not be otherwise valorised by the previously mentioned methods of treatment because of their characteristics.

Another key problem of the metal finishing industry deals with chromium. Indeed, it is a very widespread metal finishing application. It gives different properties such as hardness, aesthetics, resistance to temperature, corrosion or wear. This versatility justifies that the chromium is an essential element for various applications. The most widespread properties of the chromium metal deposit are their protective and decorative characteristics. It is estimated, at the European level, that 30 000 to 32 000 tons of chromic acid per year are used in metal finishing. Because of drag-out all along the production line, 20 to 60% are found in industrial aqueous effluents. This ratio depends on the local context of each workshop namely its size and recycling measures implemented. So, it appears that the decontamination of chromium is very important for the metal finishing industry.

2 Research Aims

For several years, many studies [5-17] have been carried out concerning the valorisation of different sludge which are either industrial (metal hydroxide sludge) or urban (activated sludge). The main application under development related to this kind of waste is the use of sludge for sorption of pollutants whether the composition is organic or mineral. It is possible to combine these applications in three categories:

- The less used or in any case the less referenced in the bibliography consists in the production of a sub-product with good sorption property for heavy metals (Hg) or toxic gas (H₂S) from a mineral sludge (heavy metals) [5] or an organic sludge [6].
- The metal hydroxide sludge generated, for example by metal finishing treatment or metallurgy, could constitute the second category of application in the pollutant sorption whether they are organic [7,8] or mineral (oxometallic anions) [9,10].
- The last application is linked to the biological activity contained in the activated sludge (organic compound, etc.). This application is highly prized by the enthusiasm of the scientific community in view of numerous publications on this subject, and is applied to all types of pollutants in water such as non-metallic anions [11,12], organic molecules [13,14], heavy metals in the form of oxometallic anions [15-17].

Generally, the versatility of applications of heavy metals in industry is such that it is difficult to generalize properties of this complex material (sludge) because chemical composition and chemical nature are different from one sector to the other. However, according to the industrial sector, it is easier to identify metals mainly used. In our case study, three transition metals are commonly used: zinc (+II), nickel (+II) and chromium (+III). The sludge used for this study is coming from two metal finishing industries whose application resides essentially in zinc, nickel and chromium plating. The metal hydroxide sludge is mainly composed of these three metals with a variation of metal composition depending on the SME activity.

The aim of this research is to allow the use of sludge as a trapping matrix of pollutants, without any other specific treatment in advance (for example incineration) and independently of their metal compositions. Considering its importance in the metal finishing treatment and in the views of its toxic properties, the pollutant chosen is chromium (+VI). Then, the aim of this project is to evaluate the influence of various parameters such as contact time, the solid / liquid ratio, temperature, grain size and chemical nature of the sludge (origin) on the sorption yield. Unlike most previous studies, the pH will be a free parameter in the sense that it will not be fixed by outside intervention (adding base or acid). Indeed, our matrix is composed of metals which can be amphoteric (Zn, Al); as a result, it could be dissolved during the experiment time if a pH adjustment was to be realized. Hence, it is better to let the pH of the solution come into balance and so to avoid a more important preferential dissolution.

3 Experimental protocol

3.1 Methods

A sludge mass "m" (mg) ranging from 50 mg to 3125 mg is put in suspension in a beaker containing a volume "V" (ml) (25 or 50 mL) of a potassium dichromate solution (Cr₂O₇²⁻) to a given concentration "C_i" (mg.L⁻¹). The system is under magnetic stirring at a temperature T (°C) (room temperature, 25°C and 35°C), for a time "t" (min) (ranging from 0 to 180 min). After this time "t", the solid is separated from the liquid phase by filtration. The liquid fraction is then analyzed by ICP (Inductively Coupled Plasma), to get the concentration "C_e" in equilibrium in total ion Cr remaining in solution. The range of initial concentrations in Cr₂O₇²⁻ (C_i) was chosen so as to comply to chromate concentrations in industrial wastewater metal finishing. This range of concentrations is from 0 to 360 mg.L⁻¹.

3.2 Raw Sludge (sorbents)

The sludge used in experimental sorption were collected in both a local SME (sludge A taken at the exit of the filter press i.e with 35% average of dry content) and a larger company (sludge B heat-treated at 1000°C beforehand). Infrared analysis, ICP analysis and X-rays

diffraction have been carried out on this sludge to define precisely the chemical nature. The ICP analysis of the sample B revealed that it was composed of several metals including three predominant ones (Zn, Ni, Cu), representing approximately 75% of metal composition. Analyzes of sludge A unveiled the presence of Zinc, Nickel and Chromium in majority. A sampling study has shown that for the sludge A the zinc composition fluctuates between 40% and 65%, the nickel composition between 5% and 10% and the chromium composition between 5% and 35%.

4 Experimental results and Discussion

4.1 Sorption kinetics of the two sludge

4.1.1 Sludge nature

According to the protocol defined in 3.1, a sorption kinetic study was realized on the two samples A and B. The experiment is conducted with 25 mL of a solution containing 30 mg.L^{-1} of Cr^{VI} and for a sludge mass of 1250 mg at room temperature (Figure 1).

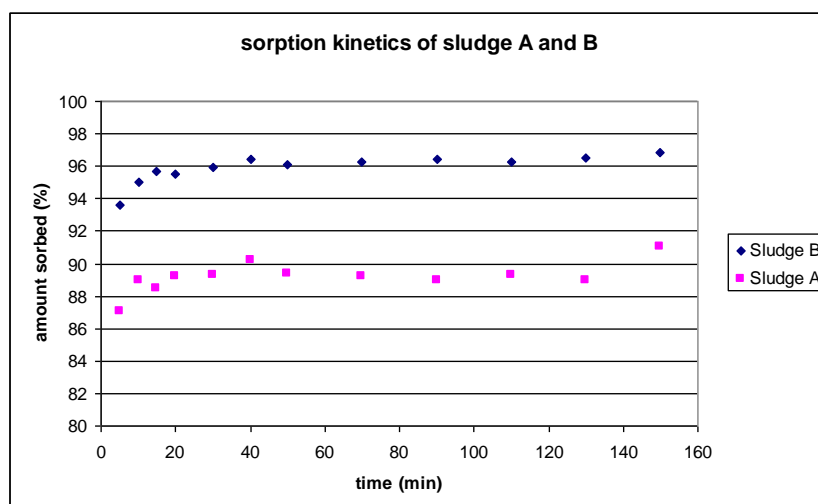


Figure 1 : Sorption kinetics of sludge A and B

Figure 1 shows that the nature of the tested sludge does not influence the kinetic sorption. The maximum sorption yield is obtained very quickly and for an experimental duration of 20min. Moreover, it is possible to observe that the chemical nature of the sludge influences it. Indeed, sludge B achieves an average sorption yield of 95% whereas for sludge A the yield is 90%. This slight difference could be explained by experimental errors. These errors are due to the mass variation of each sample ($50 \pm 2 \text{ mg}$ that is equivalent to an experimental error of 4%).

4.1.2 Sludge mass

A kinetic study based on the variation of the mass of the sludge B was realized in order to evaluate the influence of sorbent mass on the sorption yield (Figure 2). The experimental conditions are the same as 3.3.1 : 25ml of a solution containing 30 mg.L^{-1} of Cr^{VI} and at room temperature.

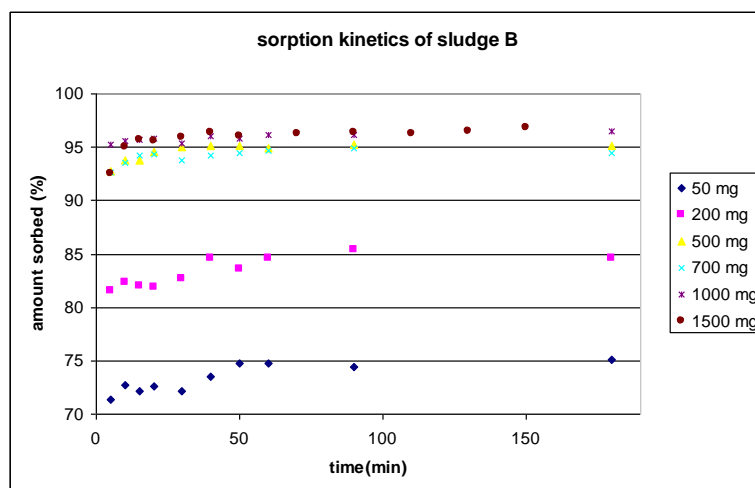


Figure 2 : Kinetics in function on sorbent mass

Figure 2 reveals that the sludge mass has a great influence on the sorption yield but not the kinetic which is always quickly. If the sorbent mass in suspension is multiplied by 30 (from 50 mg to 1500 mg), the sorption yield average goes from 75% to over 95%. Moreover, for a weight of sludge higher than 500 mg, the sorption yields are similar (average 95%). This can be explained by the fact that adding a too much important quantity of sludge in the beaker leads to a non-suspension conducting to a loss of surface contact between the liquid and solid phase.

4.1.3 [Cr^{VI}]

Part 3.3.2 highlighted that the optimal sludge mass for an optimal yield equal to 500 mg. In fact, beyond this mass, no improvement of sorption is observed. In this perspective, the protocol described before is used in setting the mass of the sludge B to 500 mg. Thus, the aim is to define the influence of a solution of Cr^{VI} on the sorption kinetics. For this, three concentrations are tested: 16, 28.8 and 73 mg.L⁻¹ (Figure 3).

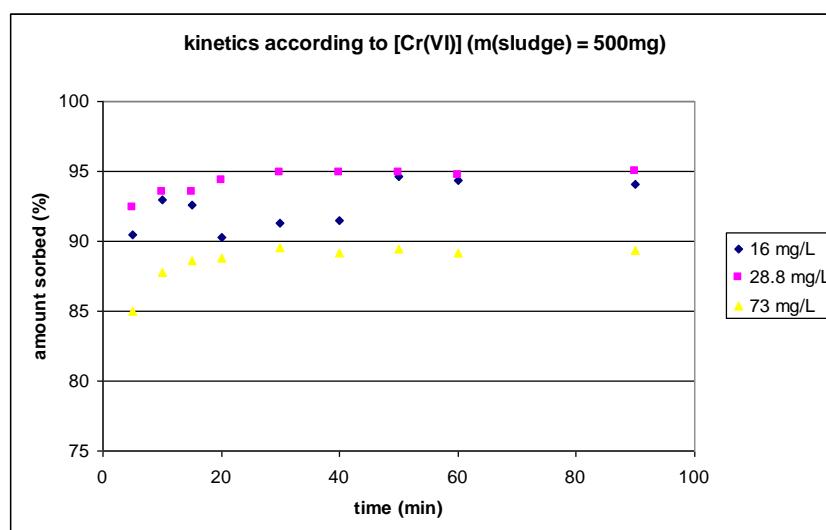


Figure 3 : kinetics according to [Cr^{VI}] to a sludge mass 500mg

Figure 3 underlines that the concentration has a slight influence on the sorption yield. For concentrations of 16 and 28.8 mg.L⁻¹, the values of the yield are quite similar and about 95%

whereas for a concentration of 73 mg.L^{-1} , it reaches 90%. For a mass of 500 mg in 25 ml of solution, a fourfold increasing of the concentration of Cr^{VI} (from 16 to 73 mg.L^{-1}) leads to a loss of 5% of the sorption yield. In fact, if sludge mass is more important than 500 mg, it could be possible to increase the sorption yield for the solution of 73 mg.L^{-1} . In fact, by adding more sludge, sorbent sites will increase and then sorption yield may reach more than 90%.

4.2 Influencing sorption parameters study

4.2.1 Temperature

The sorption experiments are done with a mass of sludge B of 50 mg in a volume of 50 mL of Cr^{VI} at concentrations ranging from 0 to 370 mg L^{-1} . The beakers are kept at a constant temperature of 25°C and 35°C and are magnetically stirred for 24 hours. The sludge B has a grain size ranging from 1 to $500 \mu\text{m}$ (Figure 4). The temperature of 35°C was chosen because it is one of the temperatures encountered in metal finishing for hot baths.

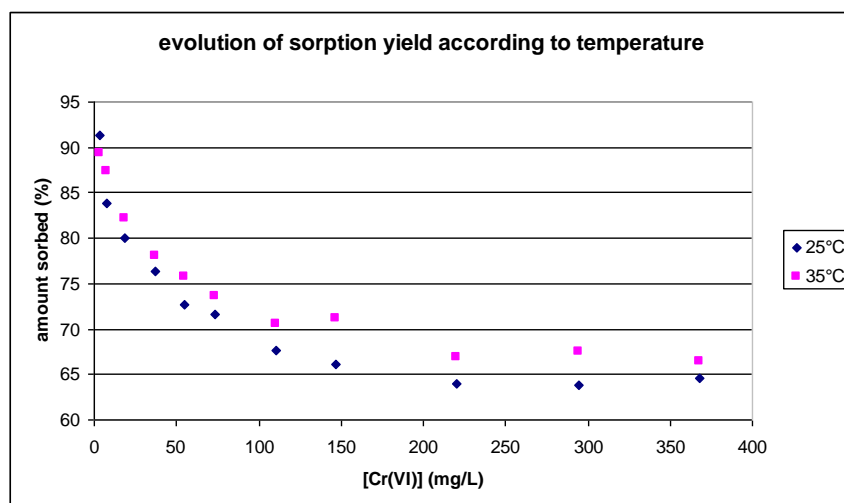


Figure 4 : Evolution of sorption yield in function of temperature

Figure 4 shows that the temperature has limited effects on the sorption yield. In some studies [24], it was highlighted that temperature only increased sorption kinetics and not sorption yield. The results obtained are normal because in our case, sorption kinetics are quick. Finally, temperatures, which are tested, (close to temperatures used in metal finishing) justify that it would not be necessary to increase the reactor temperature for an industrial application in order to improve the process.

4.2.2 Grain size

The influence of sludge grain size is tested by means of a sorption experiment on 50 mg of sludge B in 50mL of solution of Cr^{VI} at different concentrations (ranging from 0 to 370 mg L^{-1}). The beakers are kept at constant temperature of 25°C and magnetically stirred for 24 hours. The grain sizes are detailed below: a preparation was made with a mortar without sifting, another with a grain size between 1 and $500 \mu\text{m}$ and finally one with a size between 1 and $75 \mu\text{m}$ (Figure 5).

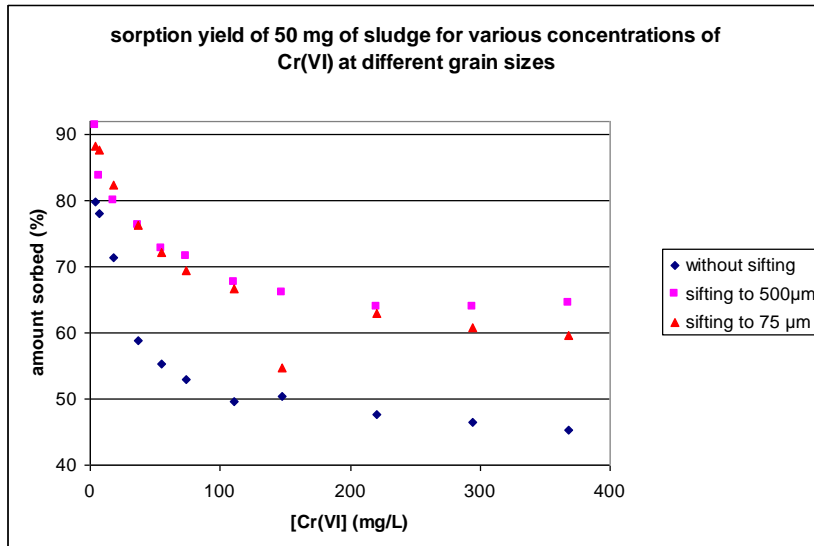


Figure 5 : Evolution of the sorption yield depending on the grain sizes

Figure 5 points out that sifting has a significant effect on the sorption yield whatever the concentration of Cr^{VI} maybe; this is especially true for the most concentrated of solutions. The difference in sorption yield between non-sifted and sifted sludge reaches about 20% for concentrated solutions. However, the sifting effect has a limit. Indeed, the range of a maximal grain size of 500 µm through 75 µm has virtually no impact on the sorption yield. So, it would be interesting to determine the optimal grain size is in order to obtain the best sorption yield because the greater the limit of grain size, the easier the sifting. This leads to a significant gain of time in the sludge preparation.

4.2.3 Moisture

The protocol used is described in 3.1. The masses of sludge A used (no dry i.e. sludge at the exit of filter press with 35% average of dry content and dry i.e. sludge dried during for seven days under extractor hood) without sifting range from 50 mg to 3125 mg and the concentration of Cr^{VI} is 30 mg L⁻¹. The sorption time is 30 minutes and takes place at room temperature under magnetic stirring (Figure 6).

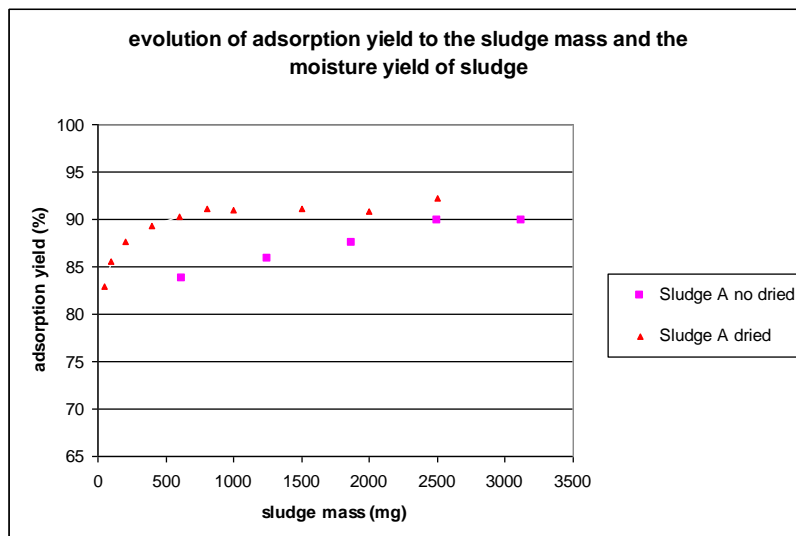


Figure 6 : Evolution of sorption yield depending on the sludge nature

Figure 6 shows that, for a given mass (2500 mg), the moisture does not influence any more the sorption yields. In fact, for a low mass of sludge, the bigger the effect of moisture, the higher the sludge mass. This result is normal because, for a low mass, the more significant the moisture, the more the yield of dry content (sorbent) is low. Therefore, this brings to a decrease of sorption yield. This effect is offset in the case of important masses because, as Figure 4 shows, there is a specific mass (or sorbent sites) beyond which no effect will be visible on the sorption yield.

4.2.4 Effects of various parameters

The whole parameters described throughout this article are presented in Figure 7. They concern only the sludge B.

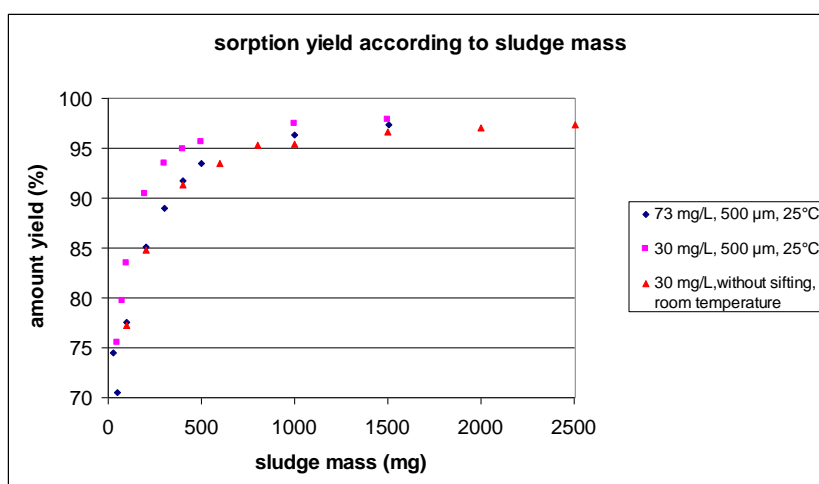


Figure 7 : Evolution of sorption yield according to some parameters

Figure 7 focuses on the fact that whatever the concentration of Cr^{VI} , the temperature, and the size of grains of sludge, for the sludge mass "m" (1500 mg here for sludge B), sorption yields are similar. This result is very important because it shows that **the sludge mass (and then sorbent sites) is THE only real parameter which influences the yield**. Besides, the results of a suitable sorption yield (95%) are closely linked to the sludge mass in suspension.

5 Conclusion

Throughout this study, it was point out that the polymetallic hydroxide sludge, from metal finishing treatment, have great sorption properties for the detoxification of an aqueous solution containing Cr^{VI} . The sorption yield may reach 95% depending on the experimental parameters. First of all, it was highlighted that the crystallinity, temperature, concentration of pollutant, humidity and the grain size have a very limited influence on sorption compared to the influence of the sludge mass in suspension. Moreover, greater the added mass, greater the mitigation of the effect of the other parameters. The kinetic sorption is quick: it is possible to consider that after 20 minutes at least, the sorption yield reaches its' maximum. The minimal time is interesting because it avoids an eventual dissolution of the sludge.

An assumption was made to justify such sorption properties of the matrix (mixed metal hydroxide) about LDH presence in sludge. At the laboratory scale, during the co-precipitation of divalent or trivalent metal at constant pH and according to experimental conditions,

Layered Double Hydroxides (LDH) could be synthesized. Their general chemical formula is $M^{2+}_{1-x}M^{3+}_x(OH)_2X^{q-}_{x/q}.nH_2O$ (at least one divalent and one trivalent metal). This is a compound family made of hydroxide sheets $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}$ where interlayered space $X^{q-}_{x/q}.nH_2O$ can be formed by different chemical species (Oxometallic anions (CrO_4^{2-} , $Cr_2O_7^{2-}$, ...), non-metallic anions,...). The sorption property of LDH stems from their structure which promotes the trapping of various pollutants (transfer of the pollutant from the aqueous phase to a solid phase). More importantly, this property is well known to the scientist community given the large number of publications on the subject [18-22]. The industrial conditions of coprecipitation are one of the major arguments in favour of the following hypothesis : in the industrial sludge production, it is possible to obtain LDH phases [23] with the metal hydroxide mixture. In spite of the lack of validation, it will be planned to identify the presence of LDH and quantify it in the industrial sludge. Moreover, we will also study the best precipitation settings in industrial conditions to yield the higher LDH in the industrial sludge in order to maximize sorption capacity. The sorption mechanism (adsorption or absorption) is being studied.

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