



# UTILIZATION OF SLUDGE RESULTED FROM CHLORINE INDUSTRY IN WASTEWATER TREATMENT

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**Keywords:** Chlorine industry sludge; heavy metals; wastewater treatment; activated brine sludge; non-activated brine sludge.

The chlorine industry sludge (CLS), which is a solid by-product resulted from the chlorine industry plants, is successfully applied as an effective adsorbent for removal of the heavy metal ions. CLS was activated by grinding to about 10  $\mu\text{m}$  particle size and burned to 700  $^{\circ}\text{C}$  for 3 h (ACLS). The physicochemical characteristics of CLS and ACLS were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM) coupled with energy dispersed X-ray analysis (EDX) unit and texture properties using  $\text{N}_2$  adsorption-desorption isotherms. CLS and ACLS are tested for removal of  $\text{Cu(II)}$ ,  $\text{Cd(II)}$  and  $\text{Pb(II)}$  from the wastewater solutions under various factors such as contact time, pH and adsorbent dose. Results showed that CLS as well as ACLS exhibit high removal efficiency of the studied heavy metal ions. These nominate them as low-cost adsorbent for  $\text{Cu(II)}$ ,  $\text{Cd(II)}$ , and  $\text{Pb(II)}$  ions.

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knowledge of their composition and characterization of their properties. Many researchers introduce brine sludge in the wastewater treatment as effective removal of heavy metal species from their wastewater solutions.<sup>8-10</sup>

The aim of this study is the reuse of CLS and activated CLS (ACLS) as a low-cost adsorbent for the removal of copper, cadmium and lead metal ions from the wastewater solutions.

## INTRODUCTION

Water resources and water supplies are a critical task which appeared recently. Only about 3 % of the water on Earth is fresh water while about 97% is salty water. Besides, more than two-thirds of the fresh water is frozen in the polar ice caps and glaciers.

Drinking water sources are contaminated by various contaminants due to the rapid industrial and civil development makes it unfit for its natural or intended uses. Contamination of drinking water sources by the heavy metals species may cause many severe health problems, diseases and in some may be fatal.<sup>1,2</sup>

The WHO gave standard regulation which specifies the limits of Total Dissolved salts (TDS), pH, metals, and other limits. Supply of clean and safe drinking water is the most crucial thing to the human life, and safe drinking water should not impose a considerable risk to humans.<sup>3</sup>

Brine Sludge is a solid by-product resulted from the chlorine industry. This solid by-products results as a precipitate from the coagulation-flocculation process from the treatment of the brine solution in the chlorine industry. The chemical composition of chlorine-sludge (CLS) have small changes depending on the source of salt which is used in the preparation of the brine solution under treatment as well as the types of chemical used in the chemical treatment, PH, temperature of the solution and the coagulant agent used.<sup>4-7</sup>

Due to the high rate and massive production of this waste many researchers tried to reuse of this solid waste material or treated it before reuse it in different applications. However, the key to reuse of these solid wastes or cycle them is the

## Experimentals

### The solid waste material:

Brine chlorine sludge (CLS) was produced during the standard chemical treatment of the brine solution in the chlorine-alkali plant (Egypt). CLS was treated as a solid residue by collecting the precipitate resulted from the coagulation-flocculation process, drying for 6 h at 110  $^{\circ}\text{C}$  then compresses at 300 bar. Activation of CLS done by grinding it to particle size 10  $\mu\text{m}$  and heating at 700  $^{\circ}\text{C}$  for 2 h.

$\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (MW: 241.6, purity: 99 % and produced by Central Drug House LTD laboratory reagent),  $\text{Cd(NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (MW: 308.48 and purity: 99% and produced by Central Drug House LTD laboratory reagent) and  $\text{Pb(NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (MW: 331.21 and purity: 99% and produced by Alpha Chemika laboratory reagent) were used for the preparation of synthetic wastewater solutions used in the present study. Solutions of (0.1 M) of each nitric acid and sodium hydroxide were used to adjust pH.

### Adsorption experiments

Batch adsorption experiments are carried out to examine the efficiency of brine sludge (activated, non-activated) for removing heavy metals ions from wastewater.<sup>11</sup> This includes the study the effect of contact time, initial solution pH, adsorbent dosage, initial metals concentration, and the

competitive metal ions were studied on the removal efficiency. The various experiments were carried out as follow:

#### Effect of contact time

0.5 g of CLS and activated CLS shacked with 50 mL of individual solutions of Pb, Cd or Cu nitrates ( $100 \text{ mg L}^{-1}$ ) in glass stopper conical flask for different time intervals; 2, 4, 6, 8, 12 and 24 hours at initial pH 5. At each time interval; filtration was carried out and the remaining concentration of each heavy metal by using inductively coupled plasma spectrometer ICP-OES Perkin Elmer Optima 8300 DV, equipped with a S10 Auto sampler and a Cetac 5000 Ultrasonic nebulizer. The removal ( $R$ ) efficiency was calculated according to the following equation.

$$R(\%) = \frac{C_i - C_f}{C_i} \quad (1)$$

where  $R$  is the of the removal efficiency and  $C_i$  and  $C_f$  are the concentration of the heavy metal ion in solution before and solution after removing process( $\text{mg L}^{-1}$ ).

#### Effect of adsorbent mass

50 mL of individual solutions of Pb, Cd or Cu nitrates ( $100 \text{ mg L}^{-1}$ ) are stirred with different dose of CLS or ACLS for 2 h at an initial solution pH 5. After 2 h, filtration was carried out, and the remaining concentration of each heavy metal was tested as mentioned above. The removal efficiency ( $R$ ) was calculated by Eq .1.

#### Effect of solution pH

0.5 g of CLS or ACLS shacked with 50 mL individual solutions of Pb, Cd or Cu nitrates ( $100 \text{ mg L}^{-1}$ ) for contact time 2 h, and initial pH of the solution was adjusted at 3, 5, 7, 9 and 11) using HCl or NaOH. Solutions pH was measured using a HACH portable pH Meter model Sens ion 156 (malty parameters). After 2 h, filtration was carried out, and the remaining concentration of each heavy metal was tested by inductively coupled plasma spectrometer. The removal efficiency ( $R$ ) was calculated by Eq .1.

#### Methods of physicochemical measurements

Phase compositions of each solid wastes used were examined using X-ray diffraction (XRD) analysis. For X-ray examination, a stabilized X-ray generator fitted with a copper target X-ray tube was used. The tube was run at 30 kV with 15 mA divergence.

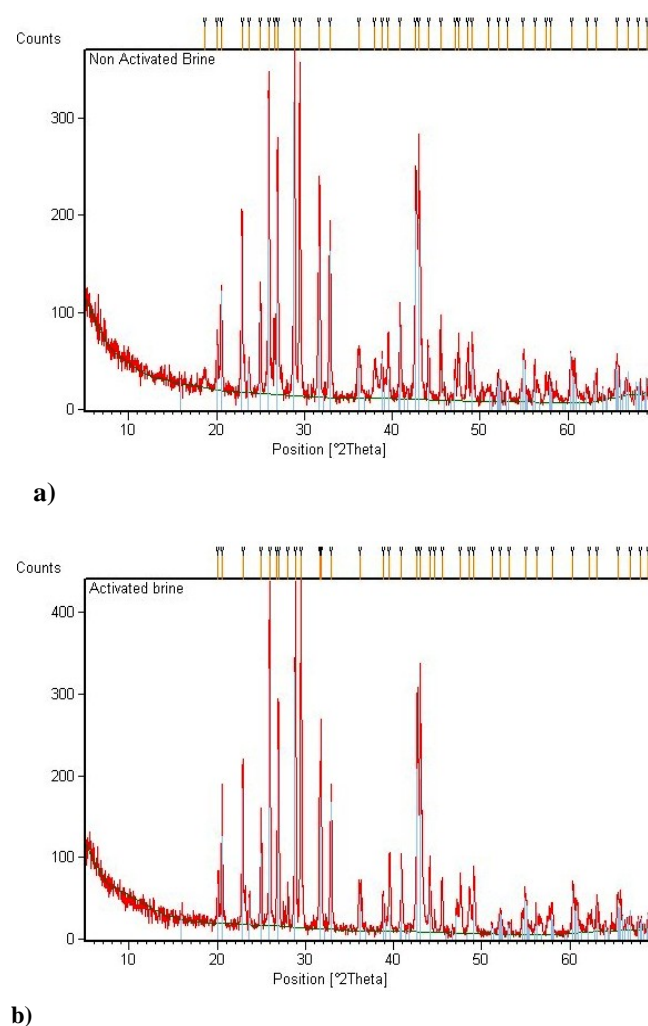
Microstructure and surface morphology verified using scanning electron microscope (SEM). This done using SEM Model Quanta 250 FEG (Field Emission Gun) attached with

EDX Unit (Energy Dispersive X-ray Analysis) with accelerating voltage 30 kV, magnification up to 1000000. The samples were covered by a thin filament of gold to improve conductivity during the examination.

## RESULTS AND DISCUSSION

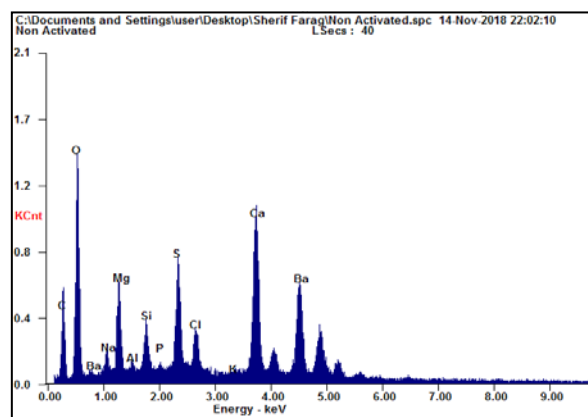
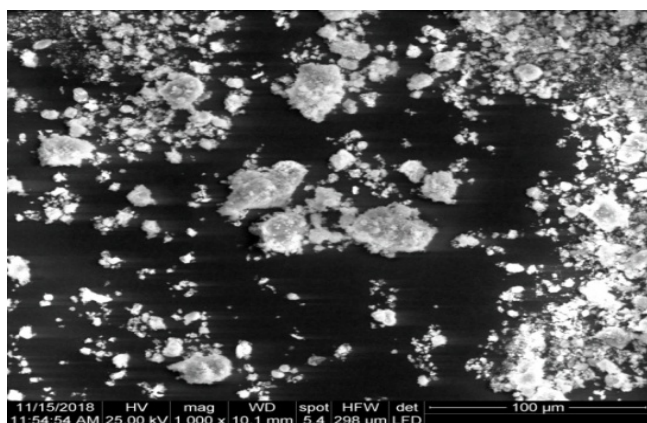
#### Characterization of solid sludge

XRD charts of both CLS and CLS burned at  $700^\circ\text{C}$  are shown in Figs. 1a and 1b. According to Fig. 1a and b; the main phases identified are illite and quartz in ACLS sample while albite phase appears only for CLS sample. Using quartz, illite and albite as an adsorbent for the removals of heavy metal ions are well known.<sup>12,13</sup>

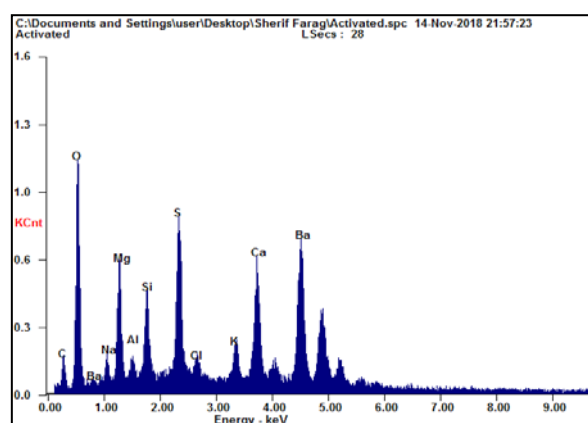
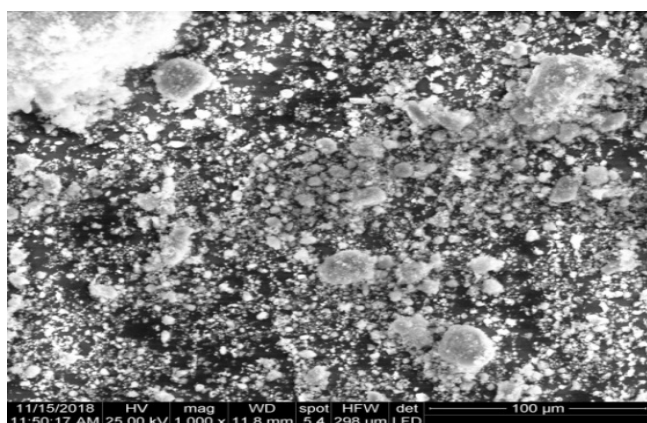


**Figure 1.** XRD analysis for CLS (a) and ACLS (b)

SEM micrograph of CLS and ACLS and EDAX are shown in Figures 2a and 2b. CLS shows a loose structure composed mainly of oxides of Si, Ca and Mg. Traces of Cl and Ba are identified in EDAX of CLS. After activation at  $700^\circ\text{C}$ , ACLS shows a more compact structure of similar oxides with an increased crystallinity and reduced chloride content.

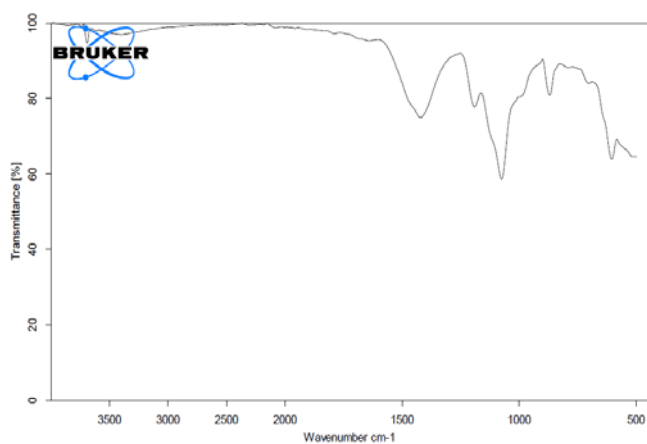


a)

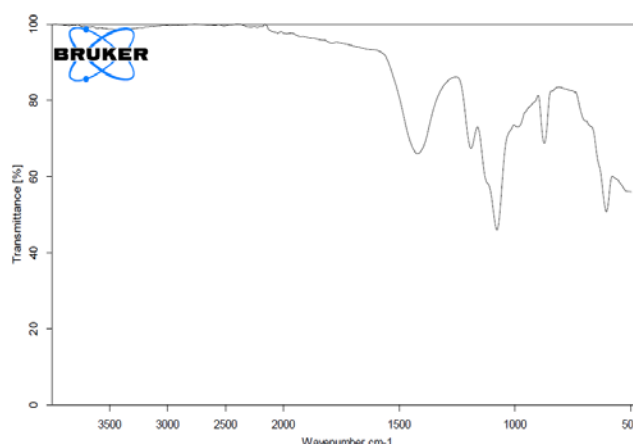


b)

**Figure 2.** SEM and EDAX analysis for a) CLS and b) ACLS



a)



b)

**Figure 3.** FTIR spectrum for a) CLS and b) ACLS

The IR spectra of CLS and ACLS samples are shown in Figs. 3a and b. The main function groups identified in FT-IR of CLS are the stretching vibration of Si=O band at 1450, and Si-O-Si at 980  $\text{cm}^{-1}$ . Thermal activation did not change these function groups as indicated by the similarities in the FT-IR spectrum of CLS and ACLS.

## Adsorption experiments

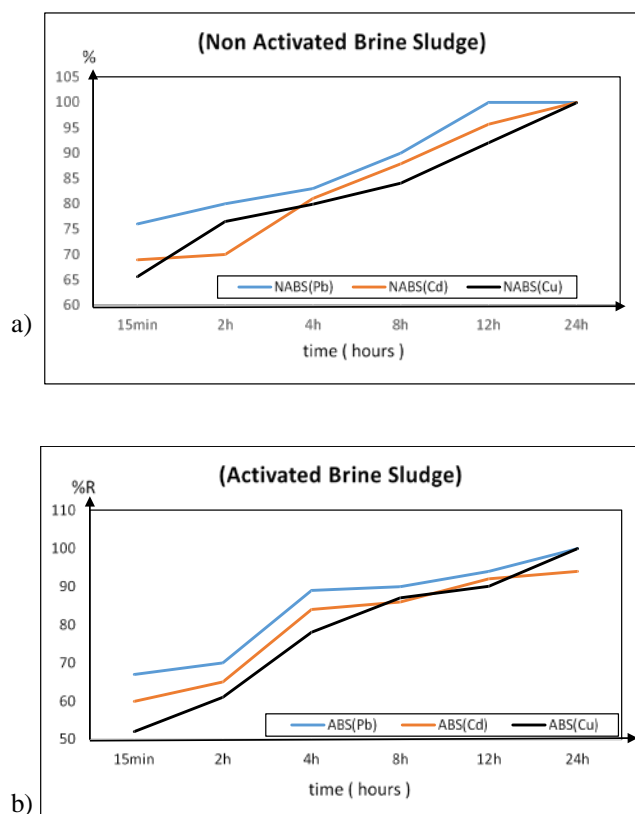
### Effect of contact time

Figs. 3a and 3b show the effect of time on the removal efficiency ( $R\%$ ) of brine sludge (activated and non-activated) for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions from wastewater. The removal

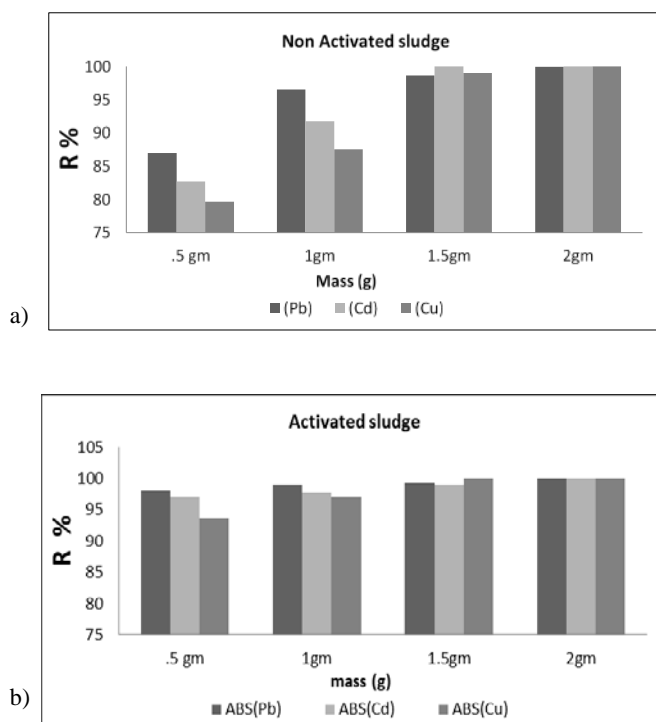
efficiency for CLS and ACLS increases with the soaking time for the three studied heavy metals ions. About 65% of the heavy metal ions are removed during the first 15 minutes and the equilibrium state reached after 24 h. Non activated brine sludge (CLS) shows removal efficiencies higher than those for activated brine sludge (ACLS) especially in case of  $\text{Cd}^{2+}$  ions.

### Effect of adsorbent mass

Effect of adsorbent mass is an important parameter which indicates the active site in the adsorbent texture. Fig 5 shows the effect of increasing the mass of brine sludge on the removal efficiency. Generally increasing the sludge mass increases the  $R\%$  value.



**Figure 4.** Effect of soaking time on removal efficiency for a) CLS and b) ACLS

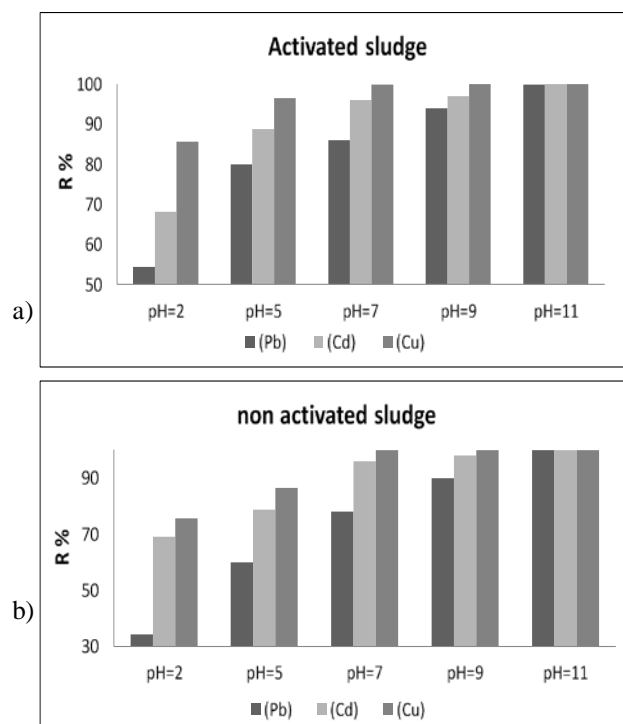


**Figure 5.** Effect of soaking time on Removal Efficiency for a) CLS and b) ACLS

Activated sludge (ACLS) shows higher  $R\%$  at low adsorbent mass 0.5 and 1 g than non-activated (CLS), especially for  $Cd^{+2}$  and  $Cu^{+2}$  ions. However, at higher mass, the removal efficiency is similar for both CLS and ACLS.

#### Effect of solution pH

Figure 6 shows the effect of solution pH on  $R\%$ . At low pH,  $R\%$  for the three studied heavy metal decreases which can be attributed to the competition between  $H^+$  and positive heavy metal ions to adsorbed in the active site on the brine sludge. Increasing the pH values to become near the neutral or alkaline values will lead to deprotonation of the acid sites on the CLS or ACLS surface and the surface becoming negatively charged with highly attractive properties.<sup>14</sup> This leads to an increase in the surface diffusion of  $M^{2+}$  ions into the adsorbent surface which highly increased the percentage of removal.



**Figure 6.** Effect of solution pH on removal efficiency for a) CLS and b) ACLS

Besides at alkaline pH,  $M^{2+}$  ions undergoes hydrolysis to  $MOH^+$  and  $M(OH)_2$  and these species have higher removal efficiency than that of  $M^{2+}$ .<sup>15</sup>  $Pb^{+2}$  ions undergo hydrolysis to  $Pb(OH)_2$  between pH 6-10 while  $Cd^{+2}$  ions precipitate as  $Cd(OH)_2$  only at pH > 7.

#### Conclusion

A sludge which is a by-product resulted from the chlorine industry plants during wastewater treatments was a useful absorbent or precursor of an absorbent for removal of the heavy metal ions such as  $Cu(II)$ ,  $Cd(II)$  and  $Pb(II)$  from the water. The high adsorption capacity of activated and non-activated brine sludge towards these ions ensures that they were proved to be low-cost adsorbent for these heavy metals.

There is no leaching effect after the adsorption which makes using the activated and non-activated brine sludge are more valuable in the wastewater treatment processes.



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