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RESEARCH ARTICLE

ALUMINA AND CHITOSAN TYPE BIO-ADDITIVE MODIFIED ELECTRONIC INDUSTRY WASTE SLUDGE FOR HEAVY METAL STABILIZATION BY MICROWAVE HEATING

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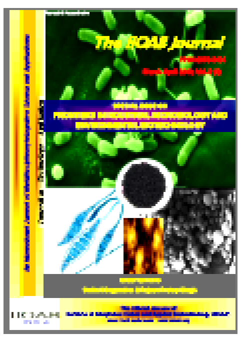
ABSTRACT



Chitosan type biopolymer is used by several researchers recently for biosorption application and dye removal in aqueous solutions. In this study, Alumina and chitosan type naturally available low cost material is used as an alternate bio-additive to stabilize the leaching toxic heavy metal ions in industrial sludge. Cement solidification is used as the common method to stabilize the industrial waste water sludge at Taiwan. However, this method has the disadvantage of an increase in waste volume. The effects of additive dosage amount, power of microwave irradiation and reaction time are studied in the present work. Heavy metal leaching capacity is determined by using standard TCLP (Toxicity Characteristic Leaching Procedure) test and elemental content in the leachate is analyzed by ICP (Inductively Coupled Plasma). Alumina and chitosan is effectively stabilizing the copper ions and control the leaching of metal ion in the presence of microwave irradiation. The optimized additive mixing in industrial sludge control the copper ions and other heavy metal ion leaching <5 mgL^{-1} upon microwave heating process in nitrogen atmosphere instead of passing air. The complete stabilization achieved for chromium and cadmium (not detected after TCLP test) compared to other heavy metal ions leaching. Finally, heavy metal ion stabilized sludge is tested for dye discoloration efficiency. Chitosan modified sludge shows the complete discoloration for the dye compounds such as methylene blue and acid red 114.

Keywords: *chitosan, microwave heating process; sludge stabilization; TCLP*

[I] INTRODUCTION

Chitosan type naturally available low cost biomolecule such as synthetic biopolymer is used by several researchers for industrial wasterwater treatment and dye removal reaction in aqueous solutions [1-3]. Chitosan is derived by deacetylation of the naturally occurring abundant polysaccharide in the world after cellulose and its show the outstanding binding behavior for pollutants removal such as dye and heavy metal ions [4]. Electronic industrial wastewater sludge with copper and other heavy metal ion content produces in a large amount of hazardous waste at Taiwan from industrial sources. Even though most of the copper ions in sludge are reclaimed by the acid-extraction process with sulfuric acid, the concentration of copper ions in the residue after the toxicity characteristic leaching procedure (TCLP) test may exceed 15 mg L^{-1}. Hence, acid-extracted industrial sludge still needs to be stabilized for heavy metal ion leaching problem. The common method for stabilizing the hazardous waste at Taiwan is cement solidification process. However, this method has the disadvantage of an increase in production of waste volume [4-7]. Hsiau and Lo [8] reported the heavy metal extractability and leacheability characteristics of chemically fixed sewage sludge and the copper and other heavy metal ions are shown the higher affinity with organics except zinc [8]. Chen et al. (2007) recently reported the various modified procedure for sludge stabilization and solidification process with the assistance of hybrid microwave irradiation heating process followed by conventional heating process [9].

Compared with other conventional thermal treatment technologies, the microwave technique with the characteristics of polar oscillation and effect of dielectric losses offers the

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advantage of selective, uniform and rapid heating [10]. The effect of microwave irradiation and cooling gas treatment in microwave heating process to stabilize the industrial sludge was studied in detail.[11] Sodium sulfide and sodium phosphate type chemical additive are used to stabilize the heavy metal ion for industrial sludge by adopting different methodology with the assistance of microwave heating as well as conventional heating effects in the past years [12-13]. Heavy metal stabilization by spinel structure formation on industrial waste sludge by suitable metal precursor and heating conditions are currently growing field of interest [14].

In order to understand the effect of additive property of alumina and chitosan to find out the optimized dosage for heavy metal stabilization in industrial electronic sludge in presence of microwave irradiation, experiments regarding the required dosage of additive, required reaction time and reaction conditions. Further, in order to reduce the use of cooling gas, several modified hybrid microwave processes were performed. The stabilization efficiency of additive modified industrial sludge is evaluated by analyzing the filtrate of the sample by US-EPA TCLP test and ICP analysis for determine the heavy metal concentration in the leachate.

[II] MATERIALS AND METHODS

2.1 Basic nature of the sludge

Sludge used for the experiments was the residue of electronics industry sludge that had gone through an acid-extraction process with sulfuric acid and from which most of the copper ions had been reclaimed. The acid-extracted sludge was dried at 105 °C until all moisture was removed. The particle size of the sludge was between 100 and 400 mesh after being crushed by a grinder. Powdery sludge was stored in a tightly closed 20 L bucket. Commercial chitosan was purchased from a chemical company in Taipei, Taiwan, and used without further purification.

2.2 Methodology and instrumentation

The potential maximum power of the industrial microwave oven employed in this study was 1600 W. A simplified diagram of the microwave oven is shown elsewhere.9 The valve on the top of the oven is to let gas out. The valve on the right is for addition of gas and was connected to a float flow meter to control the flow rate of gas. The valve on the left was connected to a vacuum pump that can provide near-vacuum conditions in the oven. A container filled with the prepared sample was placed in the center of a flat tray at the bottom of the oven. The The stabilization efficiency of additive-modified industrial sludge was evaluated by analyzing the filtrate of the sample using the U.S. Environmental Protection Agency TCLP test, and inductively coupled plasma (ICP) analysis was used to determine the heavy metal ion concentration in the leachate. Various amounts of chitosan (1.0-6.0 g) were mixed with 40 g of industrial sludge and 50 mL of deionized (DI) water for each experiment. After samples had undergone the abovementioned experimental treatments, 5.0 g of each sample was subjected to the TCLP test. The required amount of 1.0 M acetic acid solution with a pH value of 2.88 (0.05 is added with a suitable amount of sludge. The ratio of liquid to solid was 20: 1, and the rotation frequency was 30 rpm. After an extraction time of 18 h, the leachate was filtered, and the filtrate pH was adjusted to below 2. The filtrate was immediately analyzed with an inductively coupled plasma (ICP) analyzer (Jobin Yvon JY24) to prevent the formation of colloid and sediment.

[III] RESULTS AND DISCUSSION

3.1. Hybrid microwave process on α- and γ-alumina additive modified sludge

The heavy metal leaching capacity after the TCLP test for α and γ-alumina modified industrial sludge is shown in **Supplementary Table–1**. Both the microwave heating as well as conventional furnace heating effect was studied. The microwave heating time is fixed at 9 min at 600 W, after completion of microwave heating process the samples were heated further by conventional oven at two different temperatures separately such as 800 ^{o}C for one set of sample and another set of samples heated directly at 1000 ^{o}C for 6 h. The X-ray diffraction pattern of alumina modified sludge materials are studied by our group recently and the same were reported elsewhere [15]. The intensity of the peak is slightly decreased for α-alumina modified sludge samples compared to all other sample. The α-alumina modified sludge, heated at 800 ^{o}C shows the increased leaching concentration for copper ion compared to 1000 ^{o}C heat treated sample. Hence, the above point concluded that the increase in heating temperature by conventional method after the microwave heating, impact the heavy metal leaching capacity in industrial sludge.

In case of γ-alumina modified industrial sludge heated separately at 800 and 1000 ^{o}C are shown in **Supplementary Table–1**, efficient heavy metal stabilization was observed and no zinc leaching was observed. The increasing in dosage amount above 1.0 g of γ-alumina addition causing the overloading effect and results in leaching of heavy metal ion after TCLP test. The barium manganate modified sludge was mixed with 1.5 g of α and γ-alumina separately and heated in conventional heating furnace at two different temperatures **[Supplementary Table–1]**. The TCLP test of modified sludge samples are showing complete stabilization for copper and other heavy metal ions upon hybrid microwave process. The overall observation concludes that the appropriate amount of γ-alumina (1.0 g) addition with industrial sludge in presence of microwave and conventional heating process shown the efficient stabilization for industrial sludge. The γ-alumina modified industrial sludge shown the effective result for copper ion stabilization in industrial sludge in terms of less reaction time and decrease in waste volume compared to aluminum powder usage in industrial sludge treatment. The textural property and surface area of the γ-alumina is the main reason for the effective stabilization of copper and other heavy metal ion in industrial sludge compared to alumina powder mixing.

3.2. Effect of bioactive, dosage amount for electronic industry waste sludge on copper stabilization and dye decoloration activity

Effects of bioadditive, dosage amount and microwave power for copper stabilization in industrial sludge by microwave heating. **Supplementary Figure–1a** shows the copper leaching amount

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(mg L^{-1}) against different dosage of chitosan addition and **Supplementary Figure–1b** shows the effect of microwave heating time against copper leaching for modified industrial sludge at two different microwave power such as 600 W and 800 W. The increasing amount of chitosan addition decreases the copper leaching at optimized additive addition such as dosage amount, microwave power and reaction time. The lowest leaching concentration of about 2.52 mg L^{-1} was observed at 4.0 g of chitosan modified sludge treated at 800 W for 9 min and increasing the dosage amount of chitosan above 4.0 g results the copper leaching occurred **[Supplementary Figure–1a]** due to overloading of additive mixing in sludge and chitosan particle aggregation occurred. The higher microwave power like 800 W shows the effective control of copper leaching compared to low power microwave heating **[Supplementary Figure–1]**. The lowest copper leaching concentration of 4.09 mg L^{-1} is observed for 800 W microwave treatment at 6 min **[Supplementary Figure–1b]**. Hence, chitosan type bioadditive could control the copper leaching in industrial sludge by adopting optimized reaction condition such as 800 W power microwave heating at 6 to 9 min reaction time. Increasing the reaction time such as above 12 min at high power (800 W) microwave heating could cause the leaching problem.

Supplementary Table–2 shows heavy metal leaching concentration for various metal ions after the TCLP test and chitosan is completely stabilize the chromium and cadmium at 1.0 - 6.0 g of chitosan addition in sludge. Other major heavy metal ions like Zn, Cr, Cd and Ni are also shown the effective control for heavy metal leaching from sludge. The dosage amount between 4.0 g to 6.0 g of chitosan with sludge after the microwave heating shows the effective control over heavy metal ions leaching.

The modified sludge (microwave method treated heavy metal ion stabilized in chitosan mixed industrial sludge) is tested for possible sorption application related with hazardous dye discoloration experiment. Dye removal and discoloration process in the presence of biosorbent is the important topic related with wastewater treatment released from textile and chemical industries. Hence, the chitosan modified industrial sludge could act as a low cost biosorbent for dye removal as well as discoloration of the toxic dye compounds. In present study, methylene blue and acid red 114 are tested for dye discoloration activity. **Supplementary Figure–IIb** shows the filtrated solution of aqueous dye solution of mehtylene blue and acid red dye discoloration activity after 30 min of sorption experiment, increasing the sorbent weight causes the complete dye discoloration at very short time duration, due to the presence of chitosan particle in the bulk solid sludge. Chitosan itself is a popular sorbent for dye removal in wastewater treatment experiments. Hence chitosan modified sludge is tested for dye discoloration and it shows the better activity **[Supplementary Figure–IIa and IIb- No.2-5]** compared to untreated sludge **[Supplementary Figure–IIa and IIb- No.1]**. The maximum absorption wavelength for methylene blue and acid red 114 are measured at 665 nm and 522 nm, respectively. In the sorption experiment every 10 min dye solution was removed and continued the process upto 30 min and adsorbed dye solution filtered followed by analysis of the filtrate by spectrophotometer. Initially the dye adsorption efficiency is more and discoloration is very faster at the initial 10 min period and equilibration attained with in 30 min. Dye discoloration is more efficient in presence of chitosan modified materials compared to raw industrial sludge and **Supplementary Figure–IIa and IIb** shows the comparison of various amounts of sorbents in presence of dye solution.

3.3 Impact of heavy metal binding mechanism with chitosan modified bulk sold sludge

Chitosan is a basic polymer with functional groups like amino and hydroxyl groups present in its structure are playing a key role in Lewis acid base type reaction in aqueous medium. Chitosan, being a base, forms salts with acids and originates polyelectrolyte with a solubility that is a function of the nature of the anion involved and deacetylation degree. Ngah and Musa [16] reported that the adsorption of organic matter over chitosan takes place in the amino groups forming coordinated bonds, but to our knowledge just a few studies have been conducted, to understand the roll of NOM in the removal and selectivity of metal ions (such as cadmium, copper, and lead) by this biosorbent [16]. For instance, Yan and Bai [20] studied the adsorption capacity of lead onto chitosan hydrogels beads and reported that amine groups in chitosan were found to play the major role in the adsorption of lead ions or humic acids (HA), and when these two were simultaneously adsorbed their removal was significantly lower [17]. In our present work chitosan is mixed with sludge in aqueous medium and results in the possible chitosan transformation and binding reaction with heavy meat ions in the bulk sludge *via* co-ordination bond formation might occurred. The pH of the medium is playing the important role in formation of heavy metal ions binding on chitosan molecules. Several functional groups present in the chitosan molecules is involve in the possible Lewis type acid base reaction in aqueous medium with modified sludge [18]. After the microwave treatment by uniform heating effect facilitate the chitosan-heavy metal ion binding for stabilization process in the bulk sludge.

[V] CONCLUSION

The chitosan type bioadditive has been tested and successfully adopted for copper and other heavy metal ion stabilization in industrial sludge for the first time and the present methodology is not reported elsewhere. The methodology for mixing chitosan with industrial waste sludge has been developed to control the leaching of copper and other heavy metal ions. The chitosan addition dosage of 4.0 g per 40 g of solid sludge in microwave heating for 12 min at 800 W had shown the best stabilization effect for heavy metal ions. The microwave treatment at 600 W is not effective at shorter time duration (3 min) with less amount of chitosan, in the case of 800 W microwave heating treatment at longer time (15 min) duration with less amount (1.0 g) chitosan

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shows the effective stabilization for heavy metal ion in waste sludge. Hence the present study concludes that the chitosan type bio-additive mixed industrial sludge stabilize the copper and heavy metal ions effectively as well as used as an possible dye sorbent applications.

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SUPPLEMENTARY FILES

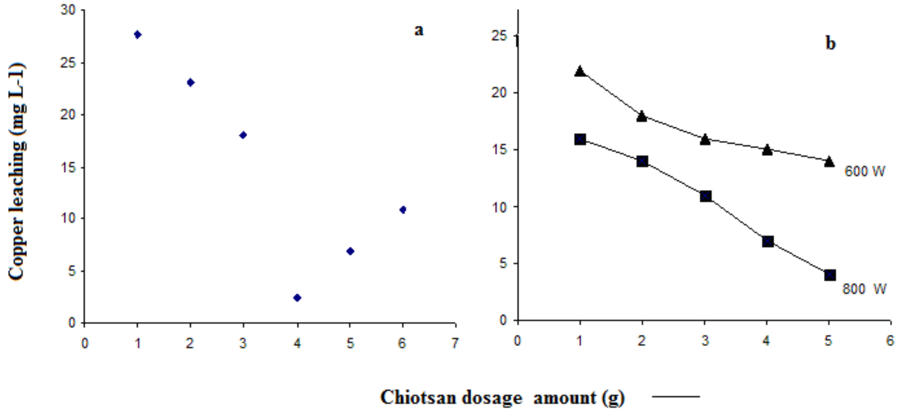
Supplementary Table: 1. Heavy metal leaching concentration of microwave heat treated alumina modified industrial sludge after TCLP test

Sludge (S)-additive Composite	pH	Zn[a]	Cr[a]	Cd[a]	Pb[a]	Ni[a]	Mn[a]	Cu[a]
At 800 °C								
S-α-alumina (0.5 g)	5.04	4.6	0.9	1.3	6.2	5.1	2.8	25.1
S-α-alumina (1.0 g)	5.60	0.9	0.6	1.3	5.8	6.0	3.9	1.8
S-α-alumina (1.5 g)	4.63	4.6	0.7	1.3	6.7	3.4	1.9	60.6
S-γ-alumina (0.5 g)	7.43	-	0.9	1.2	7.0	3.9	3.6	0.7
S-γ-alumina (1.0 g)	7.15	-	0.7	1.3	6.3	3.1	4.0	0.2
S-γ-alumina (1.5 g)	5.32	-	0.6	1.2	5.6	3.9	3.6	0.5
At 1000 °C								
S-α-alumina (0.5 g)	4.32	0.2	0.7	1.2	5.7	2.9	2.3	10.0
S-α-alumina (1.0 g)	4.37	-	0.7	1.2	5.6	2.3	1.7	5.7
S-α-Alumina (1.5 g)	4.40	-	0.6	1.2	5.6	2.3	1.7	5.3
S-γ-alumina (0.5 g)	5.70	-	0.6	1.2	5.7	2.9	4.1	5.1
S-γ-alumina (1.0 g)	5.68	-	0.7	1.3	5.8	2.9	4.3	6.2
S-γ-alumina (1.5 g)]	4.59		0.9	1.2	5.4	2.8	2.9	11.0

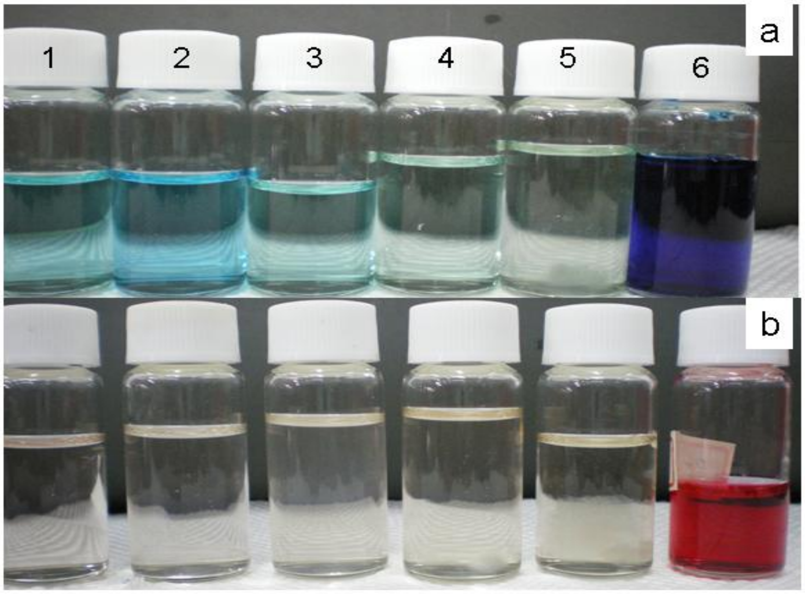
[a] all the metal ion concentration in mg L^{-1}; detection limit error ±0.05

Supplementary Table: 2. Effect of chitosan dosage on copper and other heavy metal leaching control in industrial sludge

Additive Amount (g)	Zn	Cr	Cd	Pb	Ni	Mn	Cu
1.0	29.3	0.31	0.57	3.2	6.9	7.3	27.64
2.0	28.3	0.24	0.54	2.5	6.2	6.1	23.11
3.0	28.4	0.27	0.99	2.9	6.1	6.7	18.05
4.0	27.5	0.30	0.51	3.1	3.3	4.3	2.52
5.0	0.65	-	-	0.89	2.7	2.5	6.90
6.0	1.28	-	-	1.52	2.8	2.2	10.90



Supplementary Figure (Ia) Effect of chitosan dosage amount (1 -6 g) for copper leaching control in industrial sludge **(Ib)** Effect of microwave heating power on copper leaching control.



Supplementary Figure (IIa) No. 1- 1.0 g of unmodified sludge; No. (2 – 5) - 1.0 g – 4.0 g of modified sludge ; No, 6- methylene blue solution (100 mg L^{-1}) **(IIb)** No. 1- 1.0 g of unmodified sludge ; No. 2- 5-1.0 g – 4.0 g of modified sludge ; 6-Acid red 114 (100 mg L^{-1})