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Stabilization of lead (Pb) and zinc (Zn) in contaminated rice paddy soil using starfish: A preliminary study

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1

31 **Abstract**

32

33 Lead (Pb) and zinc (Zn) contaminated rice paddy soil was stabilized using natural (NSF) and calcined starfish (CSF).

34 Contaminated soil was treated with NSF in the range of 0-10 wt.% and CSF in the range of 0-5 wt.% and cured for 28 days.

35 Toxicity characteristic leaching procedure (TCLP) test was used to evaluate effectiveness of starfish treatment. Scanning

36 electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) analyses were conducted to investigate the

37 mechanism responsible for effective immobilization of Pb and Zn. Experimental results suggest that NSF and CSF

38 treatments effectively immobilize Pb and Zn in treated rice paddy soil. TCLP levels for Pb and Zn were reduced with

39 increasing NSF and CSF dosage. Comparison of the two treatment methods reveals that CSF treatment is more effective

40 than NSF treatment. Leachability of the two metals is reduced approximately 58% for Pb and 51% for Zn, upon 10% NSF

41 treatments. More pronounced leachability reductions, 93% for Pb and 76% for Zn, are achieved upon treatment with 5 wt.%

42 CSF. Sequential extraction results reveal that NSF and CSF treatments of contaminated soil generated decrease in

43 exchangeable/weak acid Pb and Zn soluble fractions, and increase of residual Pb and Zn fractions. Results for the SEM-

44 EDX sample treated with 5 wt.% CSF indicate that effective Pb and Zn immobilization is most probably associated

45 with calcium silicate hydrates (CSHs) and calcium aluminum hydrates (CAHs).

46

47 **Keywords:** Immobilization, Heavy metals, Starfish, Sequential extraction, TCLP

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Introduction

Heavy metal contamination in rice paddy soil is a major concern because of its toxicity to human health. Pb and Zn are common heavy metals released from abandoned or closed mines in the Republic of Korea that cause rice paddy soil contamination. There are approximately 2,600 abandoned mines in the Republic of Korea and among them 1,301 mines are associated with serious heavy metal release problems (Mine Reclamation Corp., 2014). Stabilization offers a viable alternative for remediation of Pb and Zn contaminated rice paddy soils.

Traditionally, stabilization technologies have relied on two main sources of stabilizing agents, chemical products (hydrated lime, quicklime) (Jing, et al., 2004; Moon, et al., 2004) and industrial by-products (Portland cement, cement kiln dust, fly ash, etc.) (Wang and Vipulanandan, 1996; Li, et al., 2001; Dermatas and Meng, 2003; Moon and Dermatas, 2007; Moon, et al., 2008), for effective immobilization of heavy metals. Recently, attention has shifted towards low-cost, more sustainable alternatives that use natural waste materials (i.e. waste oyster shells) as stabilizing agents for immobilization of heavy metals in contaminated soils (Moon, et al., 2011; Moon, et al., 2013; Moon, et al., 2015).

Consistent to this viewpoint, this study considers use of starfish as a stabilizing agent for remediation of Pb and Zn contaminated rice paddy soil. In recent years, starfish have been recognized as a major problem leading to degradation of natural marine ecosystems. Starfish exhibit a high reproductive rate capable of laying 2-3 million eggs at a time. Additionally, starfish are known bottom feeders, capable of consuming large amounts of various benthic invertebrate organisms including ear shells, sea cucumbers, short-necked clams, shellfish, sea urchins, etc. An individual starfish organism usually consumes approximately 10 kg/yr of the above-mentioned sea organisms. Even though the triton shell is a natural predator of starfish, its population is limited and the only viable alternative for controlling outbreaks of these invasive species is capturing great numbers of starfish, often exercised by oystermen. However, marketing and recycling options for captured starfish have been scarce. Beneficial uses reported in literature include applications of starfish as a fertilizer (Park, 2003), or as additive for heavy metal removal (Hong, et al., 2011). Alternatively, starfish, a feedstock of high calcium content enhanced with various other minor elements (i.e. Mg, P, K, Zn, etc.), has recently been used as an amendment for acidic soil remediation (Lebrato, et al., 2013; Moon, et al., 2014).

The calcination process, achieved at high temperatures (900°C for 2 hours), converts calcite ($CaCO_3$), the main inorganic constituent of starfish, into quicklime (CaO). Previously, calcination at 700°C and 900°C was applied to produce calcined starfish for amelioration of acidic soil (Moon, et al., 2014). Reportedly, heavy metal immobilization with calcite and quicklime is achieved by formation of pozzolanic reaction products such as calcium silicate hydrates (CSHs) or calcium aluminum hydrates (CAHs) (Rose, et al., 2000; Dermatas and Meng, 2003; Moon, et al.,

91 2006). Therefore, it may be postulated that Pb and Zn immobilization in contaminated soil using natural state or calcined

92 starfish can be attained based on formation of pozzolanic reaction products.

93   The objective of this study is to evaluate feasibility of beneficially using starfish for immobilization of Pb and

94 Zn in contaminated soil. The effectiveness of the immobilization process was evaluated using the Toxicity

95 characteristic leaching procedure (TCLP) test (USEPA, 1992). Scanning electron microscopy-energy dispersive X-

96 ray spectroscopy (SEM-EDX) analyses were conducted to investigate the mechanism responsible for effective Pb

97 and Zn immobilization in contaminated soil treated with starfish as a stabilizing agent.

98

99 **Experimental methodology**

100

101 Contaminated soil collection

102

103 Lead (Pb) and zinc (Zn) contaminated rice paddy soil was collected from a farmland near an abandoned gold mine at

104 Jeong Eup City, Republic of Korea. This mine, active since the early 1900s, operated for extraction of gold, silver,

105 copper, and zinc until its closure in 1992. Contaminated soil was sampled at a depth of 0-30 cm from soil surface.

106 Collected soil sample was air-dried and sieved through a United States standard #10 mesh (2mm) to exclude large

107 particles and attain homogeneity. Total concentrations of Pb and Zn in contaminated soil were 980 mg·kg^{-1} and

108 890 mg·kg^{-1}, respectively. Contaminated soil was classified as sandy loam by a particle size analyzer (PSA) in

109 accordance with the United States Department of Agriculture (USDA). Soil pH was 7.22. Physicochemical and

110 mineralogical properties as well as total concentrations of Pb and Zn in contaminated soil are presented in Table

111 1. Bulk chemistry of the Pb and Zn contaminated soil measured by X-ray fluorescence (XRF, ZSX100e, Rigaku,

112 Japan) is presented in Table 2.

113

114 Stabilizing agents

115

116 The NSF used in this study were obtained from the seaside of Goseong-gun, Gyeongsangnam-do Province,

117 Republic of Korea. Initial NSF sample treatment included a multi-step rinsing using deionized (DI) water to

118 remove salty layer and other impurities. Additional treatment included air drying and grinding in a crushing mill

119 to achieve a fine, homogenized powder that passed through the United States standard #20 sieve (0.85 mm).

120 Calcination of NSF was accomplished in an electric furnace (J-FM3, JISICO, South Korea), operated at 900°C for

121 2 hours. Calcination process transformed calcite (CaCO$_3$), the main mineral NSF constituent, into quicklime (CaO)

122 (Fig. 1a-b). Major chemical composition for the NSF and CSF as determined by XRF are presented in Table 2.

123

124 Stabilization experiments

125

126 Heavy metal (Pb, Zn) contaminated soil samples were treated using 6 stabilizing-agent to soil mixing ratios for

127 NSF (0 wt.%, 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.% and 10 wt.%) and CSF (0 wt.%, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.%

128 and 5 wt.%). The 0 wt.% mixing ratios for each stabilizing agent served as control treatments for benchmarking

129 purposes. Full hydration was ensured by water content of 20% in all treated samples. All treated samples were

130 cured for 28 days in a sealed plastic container at ambient temperature (20ºC, 25% humidity). Sample designations

131 are shown in Table 3.

132

133 Analyses of chemical fractions

134

135 The sequential extraction procedure (SEP) developed by Tessier, et al. (1979) was used to investigate chemical

136 fractions of Pb and Zn in contaminated soil. This procedure allows identification of 5 distinct chemical fractions

137 designated as exchangeable (F1), weak acid soluble (F2), reducible (F3), oxidizable (F4) and residual (F5).

138 Samples of the most effective stabilization treatments (10 wt.% NSF and 5 wt.% CSF), along with control samples

139 were subjected to SEP analysis to assess differences in various Pb and Zn chemical fractions upon treatment.

140

141 X-ray powder diffraction (XRPD) analyses

142

143 X-ray powder diffraction (XRPD) analyses were conducted to investigate mineralogical changes. Sample pre-

144 treatment for XRPD analyses, included air-drying for 24 hours followed by pulverization into powder that cleared

145 the United States-standard #200 sieve (0.075 mm). A PANalytical X-ray diffraction (XRD) instrument (X'Pert

146 PRO MPD) was used for collection of step scanned X-ray diffraction patterns. A diffracted beam graphite-

147 monochromator with Cu radiation was used at 40 kV and 40 mA. The XRPD patterns were taken in the 2θ range

148 of 5-65° with a step size of 0.02° and a count time of 3 seconds per step. Jade software version 7.1 (MDI 2005)

149 and the PDF-2 reference database from the International Center for Diffraction Data database (ICDD, 2002) were

150 used for identification of mineral compositions.

151

152 SEM-EDX analyses

153

154 The treatment that produced the highest metal leachability reduction (5 wt.% CSF) was selected for SEM-EDX

155 analysis. Initial sample pre-treatment for SEM-EDX analysis included air drying. Subsequently, sub-samples were

156 placed on a double-sided carbon tape, coated with platinum (Pt) and were analyzed in a Hitachi S-4800 SEM

157 instrument equipped with an ISIS 310 EDX system.

158

159 Physicochemical analyses

160

161 Soil pH values were obtained in accordance with the KST method (MOE 2002) at a liquid-to-solid (L: S) ratio of

162 5:1 l·kg^{-1}. Effectiveness of immobilization for Pb and Zn in the contaminated soil is evaluated by TCLP test in

163 accordance with the United States EPA protocol (USEPA, 1992). Specifically, 3g of soil was mixed with 60 mL

164 of TCLP solution and agitated in a TCLP tumbler for 18 hours. Since a TCLP regulatory limit for Zn is not

165 currently in place, use of the Universal Treatment Standard (UTS) for Zn of 4.3 mg·l^{-1}, established in the LDR

166 Rules and Regulations 1999 (USEPA, 1999), is warranted for comparison purposes. Use of the UTS standard for

167 Zn has been documented in literature for a cement-based stabilization/solidification (S/S) study (Ruiz and Irabien,

168 2004) and for a cement, cement kiln dust and fly ash based S/S study (Moon, et al., 2010). Analytical

169 determinations for total Pb and Zn were made using the following procedures: 1) aqua regia [0.7 ml of HNO$_3$

170 (65%, Merck) and 2.1 ml of HCl (37%, J.T. Baker)] addition to the soil sample (0.3 g) (MOE 2010); 2) mixture

171 heating at 70°C for 2 hours and dilution with 7.2 ml of distilled water (MOE, 2010); 3) filtration of extracted

172 solution through a 0.45-μm micropore filter; 4) analytical determination of filtrate soluble Pb and Zn

173 concentrations using an inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 8300DV)

174 (PerkinElmer, CT, USA). ICP-OES was used for determination of TCLP Pb and Zn concentrations. All ICP-OES

175 determinations were conducted in duplicate or triplicate, and mean values were reported within 10% error. Three

176 different quality control standards were used for every 20 samples analyzed to ensure QA/QC.

177

178 **Results and discussion**

179

180 Soil properties

181

182 Following 28 days of curing, the soil pH and organic contents were increased. The soil pHs upon 2-10 wt.% WOS

183 treatments ranged from 8.42 to 8.51. Moreover, the soil pHs upon 1-5 wt.% COS treatments ranged between 10.94

184 to 12.45. The soil pH increase was more pronounced upon COS treatment, due to high CaO content. The organic

185 contents upon WOS and COS treatment ranged from 3.77 to 3.94 and 3.21 and 3.47, respectively. The organic

186 content upon COS treatment was not notable due to the very low organic content of COS itself (0.87%).

187

188 XRPD analyses

189

190 X-ray powder diffraction (XRPD) analyses of the contaminated soil, presented in Table 1, reveals that quartz,

191 muscovite and albite are the main mineral phases. XRPD analyses revealed that the main phase in NSF is calcite

192 [(Ca, Mg) CO_3, PDF# 43-0697] mainly transformed into quicklime (CaO, PDF# 48-1467) in the CSF upon

193 calcination conducted at 900°C for 2 hours (Fig. 1).

194

195 Effectiveness of the stabilization treatment

196

197 TCLP Pb and Zn concentrations with the TCLP pH values of samples subjected to NSF and CSF treatment are

198 presented in Figs. 2 and 3. In NSF treated samples (Fig. 2a), TCLP Pb concentrations decreased with increasing

199 NSF content. Evidently all treatments at levels 4 wt.% NSF or higher produce Pb levels compliant to the TCLP

200 regulatory limit of 5 mg·l^{-1}. The lowest TCLP Pb concentration of 2.87 mg·l^{-1}, attained upon treatment with 10

201 wt.% NSF, represents a decrease of more than 58% in TCLP Pb concentration compared to the control sample. At

202 this point, it should be noted that NSF treatments at levels greater than 6 wt.% may not be warranted as they did

203 not produce commensurate reduction of TCLP Pb levels. It has been reported that a significant reduction (100%)

204 in TCLP Pb concentration was achieved in an 81 mg/L control sample, upon 10 wt.% NSF treatment (Lim, et al.,

205 2017). High reduction rate reported by Lim, et al. (2017) may depend on variability of starfish, soil characteristics

206 and the Pb form in the control and treated samples. Much like the TCLP Pb results, the TCLP Zn concentrations

207 (Fig. 2b) decreased with increasing NSF content. However, although all NSF treatments produced Zn level

208 reductions 50% or higher compared to the control, none was compliant to the UTS standard for Zn of 4.3 mg·l^{-1}.

209 The 10 wt.% NSF treatment produced marginally the lowest TCLP Zn concentration of 7.4 mg·l^{-1}. TCLP Zn level

210 reductions as high as 100% in the 6.5 mg/L control sample upon 10wt.% NSF treatment have been reported in

211 literature (Lim, et al., 2017). Higher reductions reported by Lim, et al. (2017), may be associated with variability

212 of starfish, soil characteristics, and the Zn form in control and treated samples.

213   In CSF treated samples (Fig. 3), reduction in TCLP Pb leachability (Fig. 3a) was more pronounced than that of

214 the NSF treated samples. 2 wt.% CSF was sufficient to ensure compliance with the TCLP regulatory limit of 5

215 mg·l^{-1}. The lowest TCLP Pb concentration of 0.46 mg·l^{-1}, attained upon 5 wt.% CSF treatment, represents a

216 reduction in TCLP Pb leachability of more than 93% compared to the control. A comparable TCLP Pb reduction

217 of 100% attained upon 5wt.% CSF treatment has been reported (Lim, et al., 2017). Similarly, the TCLP Zn

218 concentrations were significantly reduced upon CSF treatment compared to those obtained with NSF treatment.

219 This indicates that CSF treatment was more effective than NSF treatment and is evident by the lower TCLP Zn

220 concentrations for all treatment levels compared to those of NSF treatment. The lowest TCLP Zn concentration of

221 3.61 mg·l^{-1} attained upon 5 wt.% CSF treatment complied with the UTS standard for Zn of 4.3 mg·l^{-1}. It has been

222 reported that TCLP Zn reduction of 100% was observed upon 5 wt.% CSF treatment (Lim, et al., 2017). Based on

223 these results, it can be concluded that CSF treatment is highly effective in immobilizing Pb and Zn in contaminated

224 soils at relatively low dosage levels. This finding is corroborated by Lim, et al. (2017) that observed CSF treatment

225 was more effective than the NSF treatment. Based on results of SEM-EDX analyses, it can be postulated that

226 formation of pozzolanic reaction products, such as calcium silicate hydrates (CSHs) and calcium aluminum

227 hydrates (CAHs), are most likely responsible for Pb and Zn immobilization.

228

229 Sequential extraction results

230

231 Results of the SEP analysis are presented in Fig. 4. Since untreated and treated soil samples vary significantly in

232 terms of basic physicochemical properties and mineral composition, results of the SEP analysis of the soils are

233 used to theorize on relative binding strength of Pb and Zn. Upon 10 wt.% NSF treatments, exchangeable (F1) and

234 weak acid soluble (F2) fractions for Pb and Zn decreased. Reducible (F3), oxidizable (F4) and residual (F5)

235 fractions increased for Pb upon NSF treatment. In this case, Zn F4 and F5 fractions increased. Similarly, upon 5

236 wt.% CSF treatment, the F1 and F2 fractions for Pb and Zn significantly decreased. This reduction was more

237 pronounced as compared to the 10 wt.% NSF treatment. In the case of Pb, the F3, F4 and F5 fractions significantly

238 increased. It has been reported that in the case of Pb, decreases in F1 and F2 fractions were associated with increase

239 in the F3 fraction upon calcined oyster shell (COS) and coal mine drainage sludge (CMDS) treatment (Lee, et al.,

240 2013). This mixed treatment was like the CSF treatment since the main phase in COS was CaO. Lee, et al. (2013)

241 reported that changes in the fractions from F1, F2 and F3 supported the stabilization effect on Pb. In the case of

242 Zn, the F3 and F5 fractions increased but the F4 fraction was virtually similar. This suggested that reduction in the

243 F1 and F2 fractions and increase in the F3, F4 and F5 fractions for Pb are most probably associated with high

244 degree of stabilization achieved with NSF and CSF. In the case of Zn, reduction in F1 and F2 fractions and increase

245 in the F5 fraction was most probably linked to the high degree of stabilization achieved with NSF and CSF.

246

247 SEM-EDX results

248

249 SEM-EDX and mapping results for the 5 wt.% CSF treated sample are presented in Fig. 5. Pb and Zn were

250 identified by the SEM-EDX analysis (Fig. 5a). The Si content, displayed by the white color in the mapping results,

251 in all areas was very high. Even though low signals for Pb and Zn were detected due to low total contents, these

252 signals were strong in the targeted particle. Therefore, the elemental dot map results reveal that Pb and Zn

253 immobilization was most probably associated with Ca, Al, Si, and O due to the formation of pozzolanic reaction

254 products such as CSHs and CAHs (Fig. 5b). Support for this finding is well documented in literature. Reportedly,

255 Pb is immobilized within the CSH matrix by direct linkages at the end of silicate chains via Pb$-$O$-$Si bonds (Rose,

256 et al., 2000). Pb incorporation into the CSH structure has been reported as the key mechanism for effective Pb

257 immobilization using quicklime (Dermatas and Meng, 2003). In addition to previous research, specific types of

258 CSHs such as, $CaH_4Si_2O_7$ and $Ca_5Si_6O_{16}(OH)_2$ were identified as phases strongly associated with effective Pb

259 immobilization upon quicklime treatment (Moon, et al., 2006). It has been reported that ettringite formation was

260 identified as responsible for Pb immobilization in a 10 wt.% CSF treated sample (Lim, et al., 2017). However,

261 ettringite was not observed in the 5 wt.% CSF treated sample because samples did not contain significant sulfate

262 levels. Therefore, ettringite may not be the phase linked to effective Pb immobilization. Ettringite,

263 $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (Aft) or $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$, is a key pozzolanic reaction mineral product (Moon, et

264 al., 2010) that can immobilize Pb inside of the ettringite crystal matrix by solid solution with Ca^{2+} (Gougar, et al.,

265 1996). Effective Zn immobilization may be achieved by a tricalcium silicate component (Bhatty, 1987) or CSHs

266 compounds. Zn incorporation into CSH strucutre has been reported to proceed either by replacement of Ca^{2+} or by

267 direct linkage to the end of silicate chains through Zn-O-Si bonds (Moulin, et al., 1999; Rose, et al., 2001).

268

269 **Conclusion**

270

9

In this study natural (NSF) and calcined starfish (CSF) were used to immobilize Pb and Zn in contaminated rice paddy soil. The stabilization treatment results revealed that NSF and CSF treatments were effective in reducing TCLP Pb and Zn leachability. The CSF treatment outperformed the NSF treatment. In order to comply with the TCLP Pb regulatory limit of 5 mg·l^{-1}, 4 wt% NSF and 2 wt% CSF were required, respectively. In the case of Zn immobilization, all NSF treatments failed and 5 wt% CSF was needed to pass the UTS standard for Zn at 4.3 mg·l^{-1}. Chemical fraction analyses revealed that the effective Pn and Zn immobilization upon NSF and CSF treatment was strongly associated with the residual phase. The SEM-EDX and mapping results indicated that pozzolanic reaction products such as CSHs and CAHs may be the most probable compounds associated with effective Pb and Zn immobilization.

Acknowledgement

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363 **Table 1** Physicochemical and mineralogical properties and total concentrations of heavy metals in the soil.

Soil properties	Contaminated Soil	Korean warning standards[a]
Soil pH	7.22	
Organic matter content (%)[b]	3.16	
Composition (%)[c]		
Sand	66.3	
Silt	13.5	
Clay	20.2	
Texture[d]	Sandy loam	
Heavy metals (mg·kg^{-1})		
Pb	980	200
Zn	890	300
Mineral compositions[e]	Quartz	
	Albite	
	Muscovite	

364 [a]Korean warning standards for soils in residential areas.

365 [b]Organic matter content (%) was calculated from measured loss-on-ignition (LOI) (Ball 1964; FitzPatrick 1983).

366 [c]Soil classification was conducted using a particle size analyzer (PSA); Sand, 20-2,000 μm; silt, 2-20 μm; clay,

367 <2 μm.

368 [d]Soil texture as suggested by the United States Department of Agriculture (USDA).

369 [e]Mineral compositions were obtained using the Jade software (MDI 2005).

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383 **Table 2** Major chemical composition of contaminated soil and starfish (wt.%).

	Contaminated soil	NSF	CSF
Chemical composition (wt.%)			
SiO_2	71.3	4.87	4.63
Al_2O_3	15.8	1.51	1.07
Fe_2O_3	3.34	0.39	0.50
K_2O	3.19	1.57	1.46
CaO	1.07	38.7	70.7
MgO	0.92	2.30	9.25
TiO2	0.51	0.05	0.03
P_2O5	0.20	1.13	1.21
pH (1:5)	7.22	7.14	12.52
LOI	3.16	39.9	0.87

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405 **Table 3** Treatability matrix for Pb and Zn contaminated soil.

Sample ID	Contaminated soil (100 wt%)	NSF (wt%)	CSF (wt%)	L:S ratio (l kg^{-1})
Control	√	0	-	20:1
2% NSF	√	2	-	20:1
4% NSF	√	4	-	20:1
6% NSF	√	6	-	20:1
8% NSF	√	8	-	20:1
10% NSF	√	10	-	20:1
1% CSF	√	-	1	20:1
2% CSF	√	-	2	20:1
3% CSF	√	-	3	20:1
4% CSF	√	-	4	20:1
5% CSF	√	-	5	20:1

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427   **Fig. 1.** XRPD patterns for NSF and CSF.

428   **Fig. 2.** (a) TCLP Pb and (b) TCLP Zn results for NSF treated samples; curing period 28 days.

429   **Fig. 3.** (a) TCLP Pb and (b) TCLP Zn results for CSF treated samples; curing period 28 days.

430   **Fig. 4.** Chemical fractions of Pb and Zn for (a) the control and 10 wt.% NSF treated samples and (b) the control

431   and 5 wt.% CSF treated samples.

432   **Fig. 5**. SEM-EDX analyses and element dot maps for (a) Pb and (b) Zn in contaminated soil treated with 5

433   wt.% CSF.

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457 **Fig. 1.**

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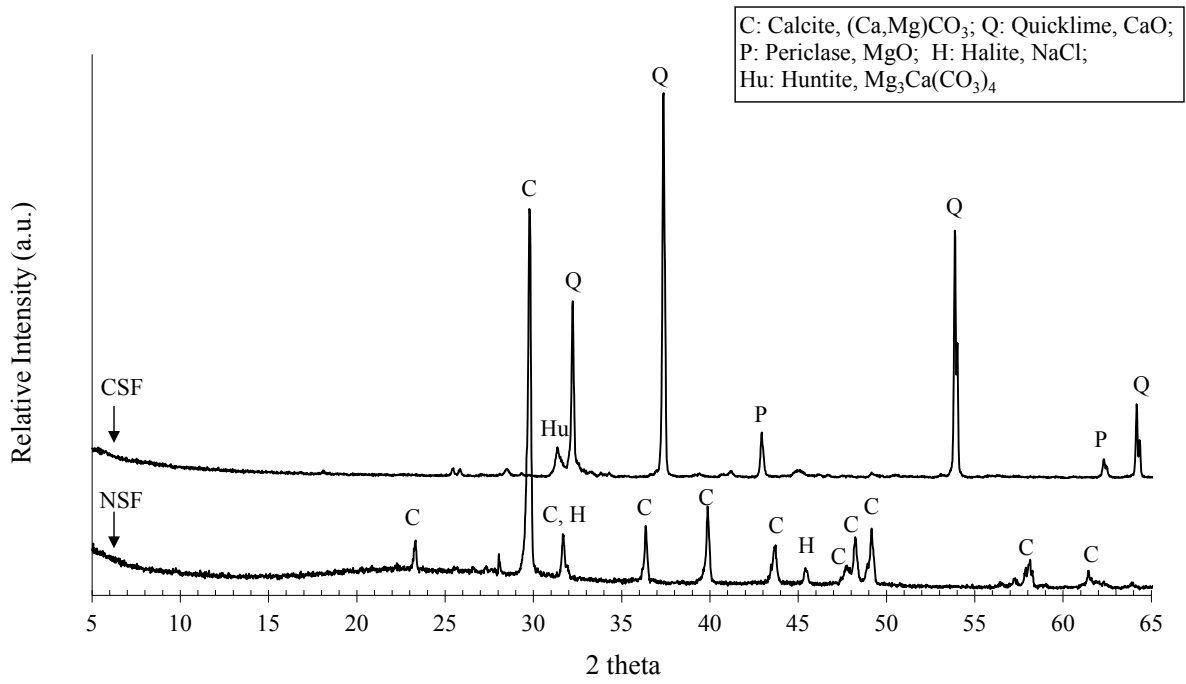
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476   **Fig. 2.**

477   (a)
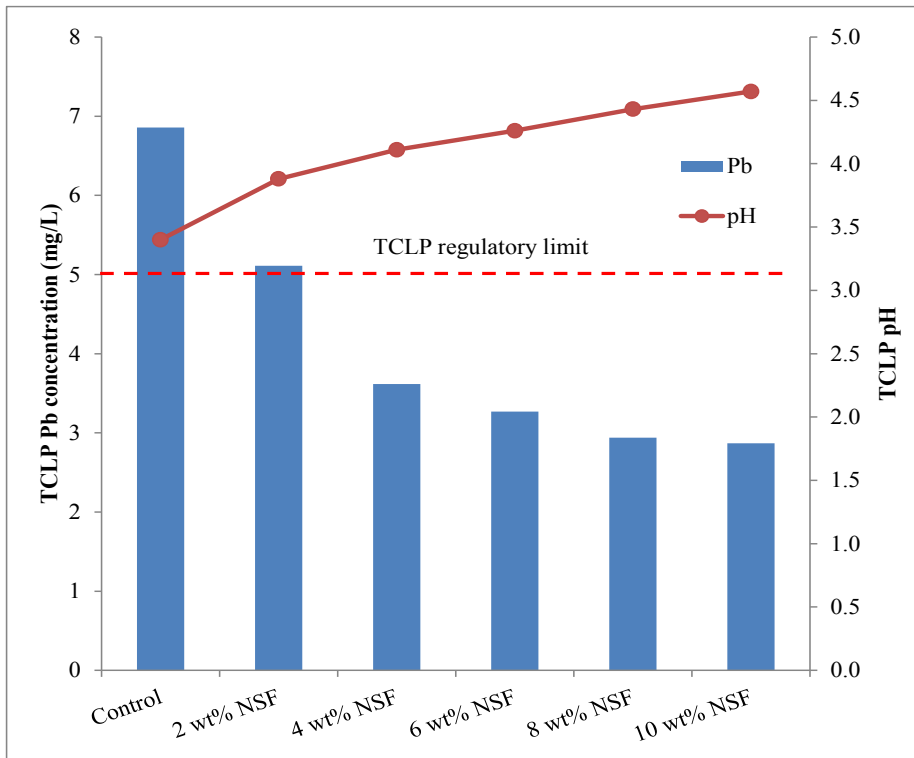
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479   (b)
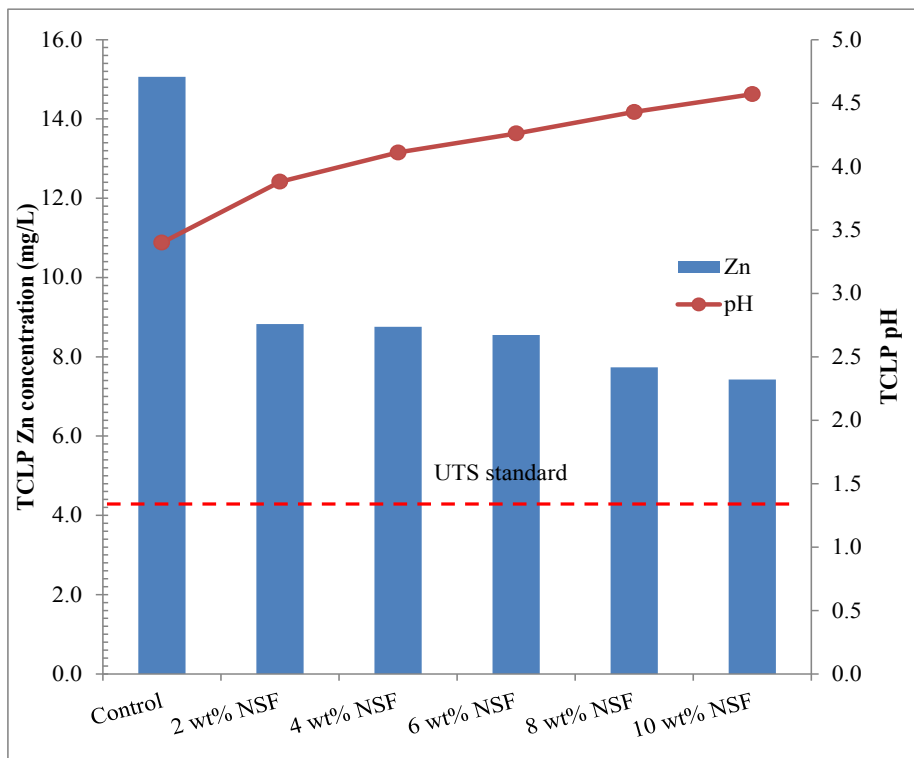
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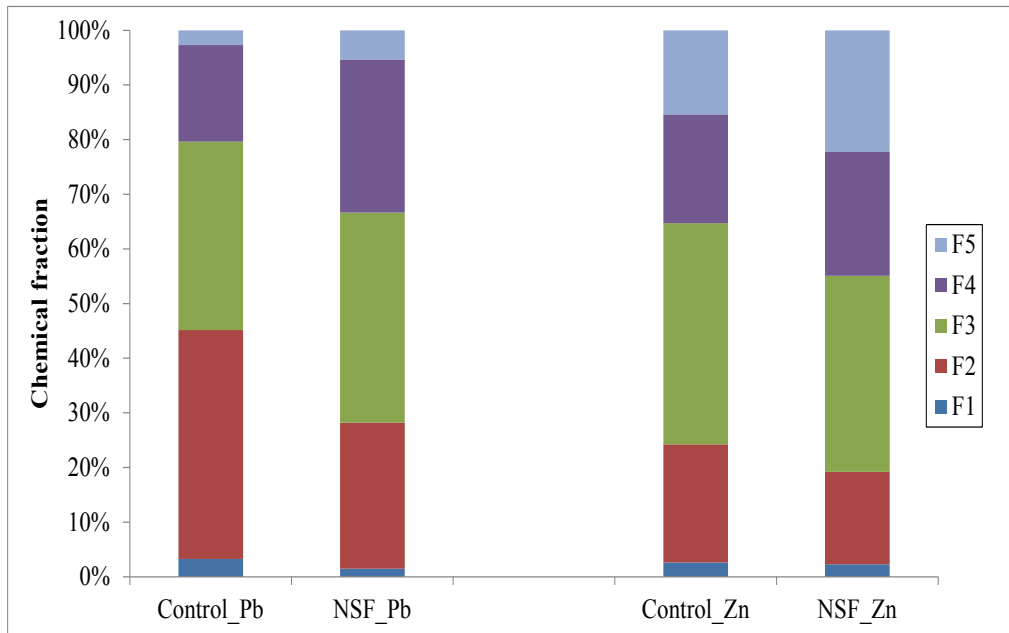
483 **Fig. 3.**

484 (a)
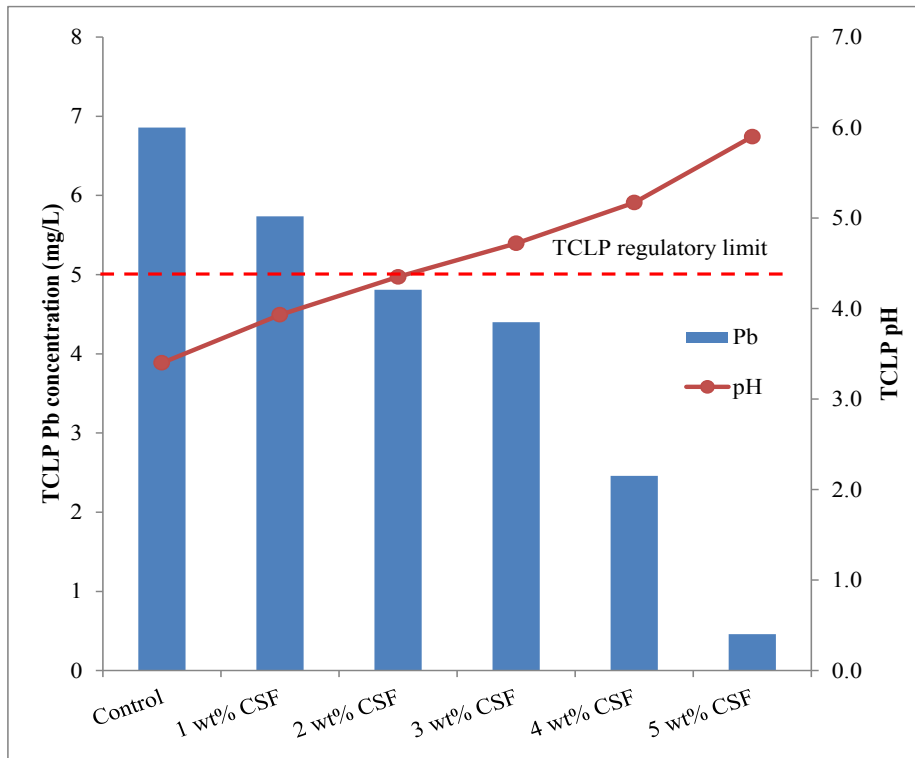
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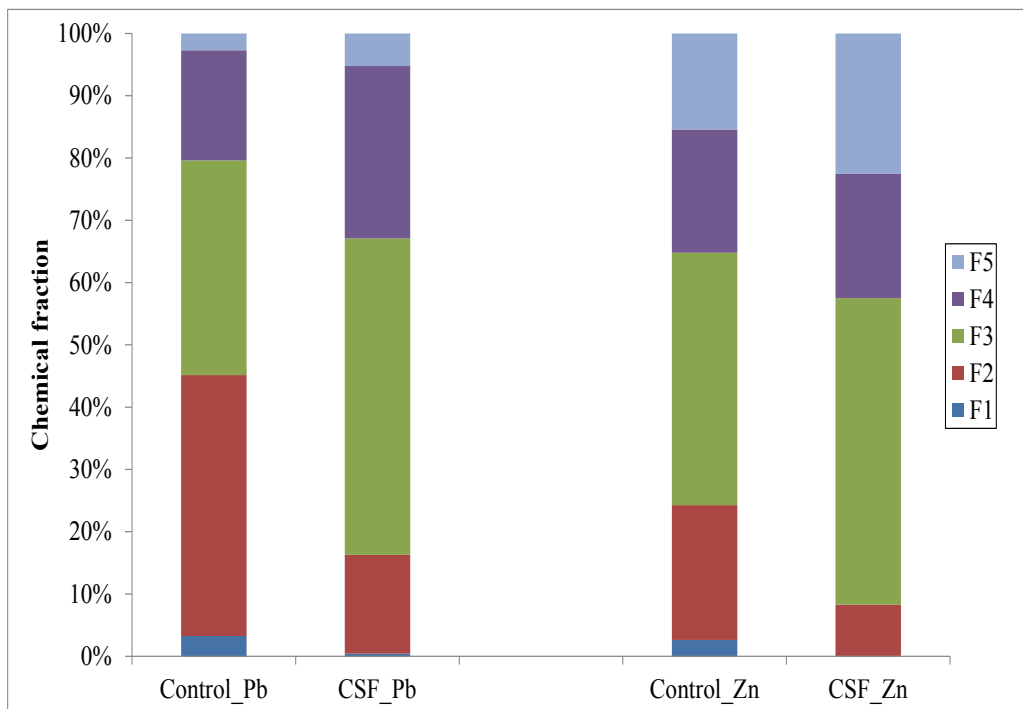
486 (b)
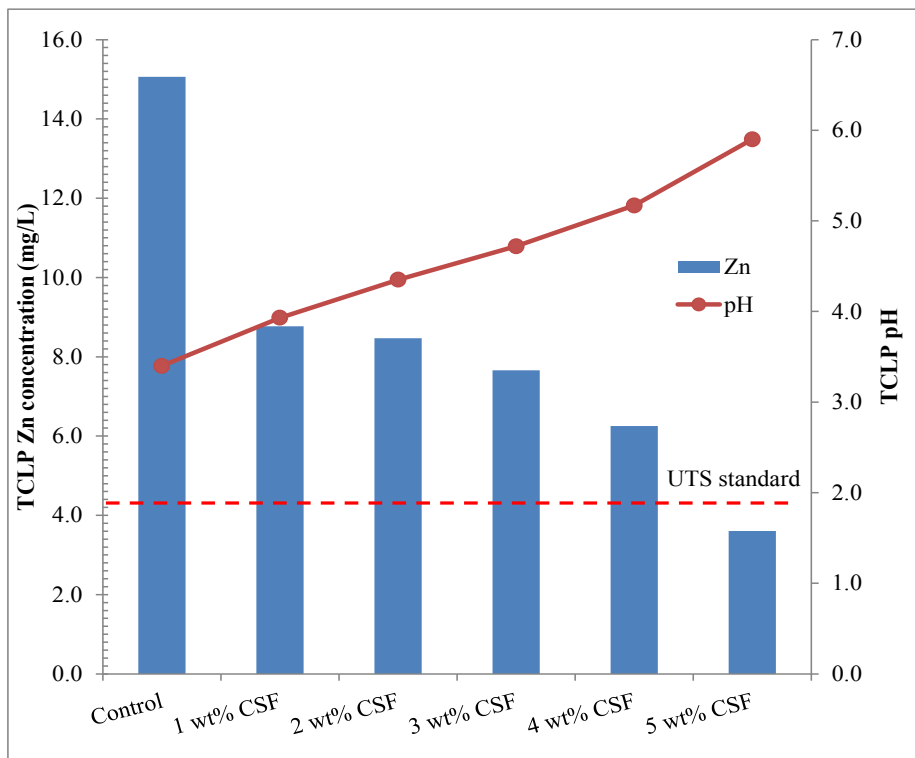
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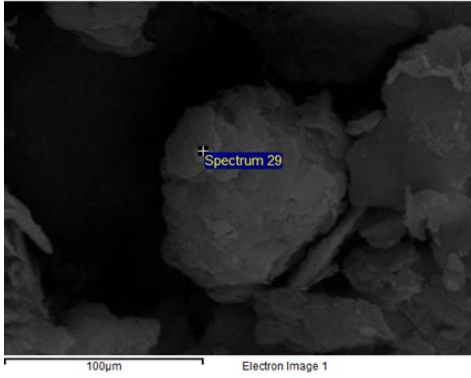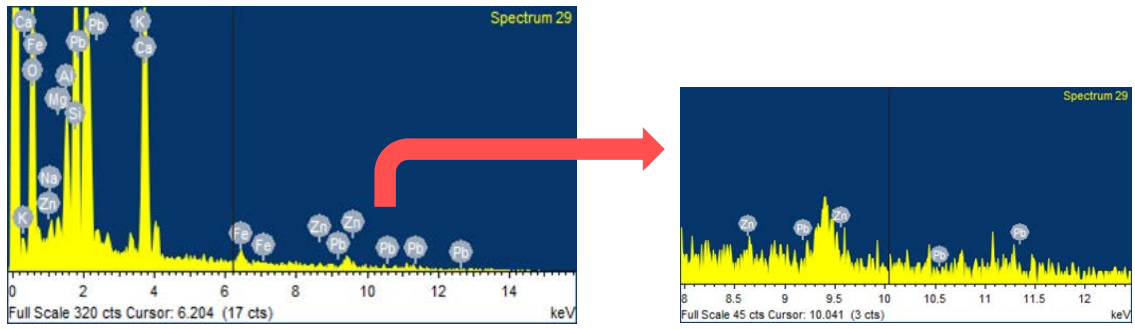490   **Fig. 4.**

491   (a)

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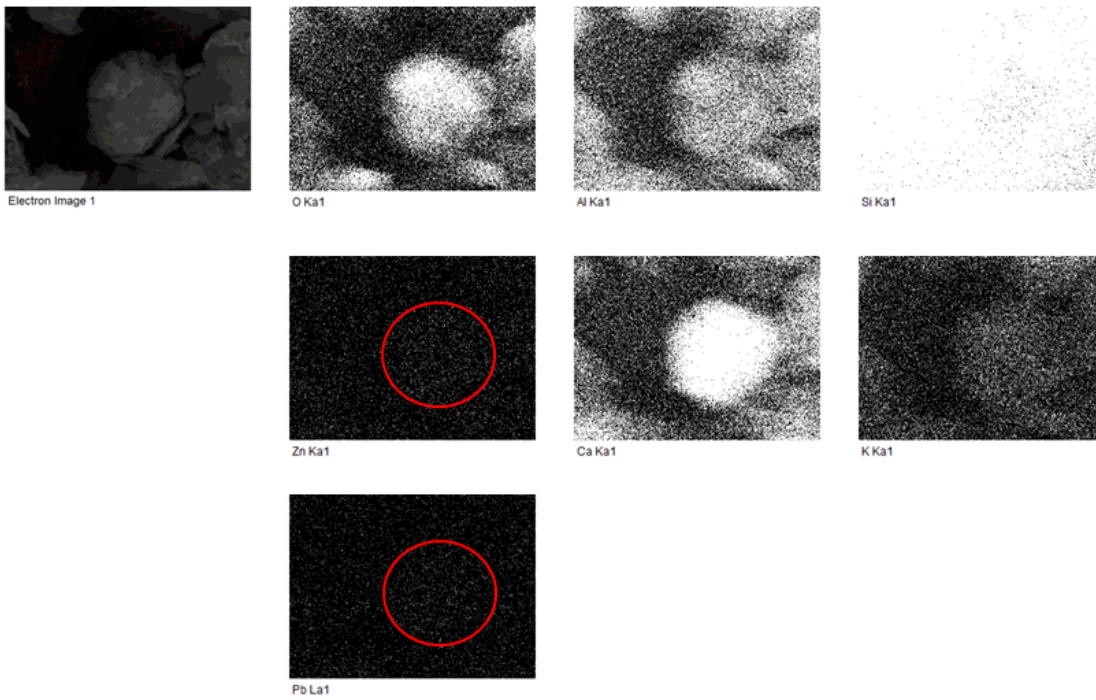
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494   (b)

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500 **Fig. 5.**

501 (a)

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504 (b)

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