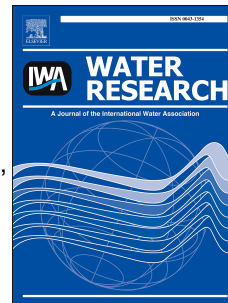# Accepted Manuscript

Potential for use of industrial waste materials as filter media for removal of Al, Mo, As, V and Ga from alkaline drainage in constructed wetlands - adsorption studies

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Regulation of pH

Alkaline drainage high in Al, Ga, V, As, Mo

Alum water treatment sludge or bauxite

Wastewater low in inorganic contaminants

Adsorption/precipitation reactions

Potential for use of industrial waste materials as filter media for removal of Al, Mo, As, V and Ga from alkaline drainage in constructed wetlands - adsorption studies

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ABSTRACT

The potential to remove Al, Mo, V, As and Ga from alkaline (pH 8.0-8.6) drainage originating from seawater neutralized bauxite processing residue storage areas using constructed wetland technology was studied in a laboratory study. Bauxite processing residue sand, bauxite, alum water treatment sludge and blast furnace slag were investigated as potential active filter materials. Al was shown to precipitate as $Al(OH)_3$ in the pH range 7.0-8.0 in aqueous solution and 6.0-8.5 in the presence of silica sand particles that provided a surface for nucleation. For V As Mo and Ga, adsorption to the surfaces of the adsorbents decreased greatly at elevated pH values (> pH 6-9). Water treatment sludge and bauxite had a greater ability to adsorb V, As and Mo at high pH (As and V at pH 7-9 and Mo at pH 5-7) than processing sand and slag. Adsorption isotherm data for As and V onto all four adsorbent

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29

30 than processing sand and slag. Adsorption isotherm data for As and V onto all four adsorbent

31 materials fitted equally well to the Langmuir and Freundlich equations but for Ga, and to a

32 lesser extent Mo, the Freundlich equation gave higher R^2 values. For all four ions, the

33 maximum adsorption capacity (Langmuir value q_{max}) was greatest for water treatment sludge.

34 Bauxite adsorbed more Mo, Ga and V than residue sand or slag. The pseudo-second order

35 equation gave a better fit to the experimental kinetic data than the pseudo-first order model

36 suggesting that chemisorption rather than diffusion/exchange was the rate limiting step to

37 adsorption. It was concluded that water treatment sludge and bauxite were the most effective

38 adsorbents and that for effective removal of the target ions the pH of the drainage water needs

39 to be decreased to 6.0-7.0.

40 Keywords: bauxite residue mud, Al, Mo, As, V, Ga, wastewater, alkaline drainage, water treatment

41 sludge, bauxite

42

43

44 **1. Introduction**

45 Bauxite ore is mined and refined using the Bayer process in which Al-containing minerals are

46 dissolved in hot NaOH. For each tonne of alumina, 1-2 tonnes of insoluble solids (bauxite

47 processing residue) are produced and these are usually deposited in land-based lagoons or

48 impoundments surrounding the refinery. Bauxite residues have a high pH (11-13) and possess

49 high salinity and sodicity (Jones and Haynes, 2011). As a result, drainage from storage areas

50 can pose an environmental risk and must be managed and drainage may need to be treated for

51 many decades after closure. For this reason, an increasing number of refineries are now

52 partially neutralizing their residues before they are deposited in storage areas and seawater

53 neutralization is used by several refineries situated close to the marine environment. By

54 addition of Ca and Mg in seawater, alkaline buffering anions in the residue are neutralized by

2

55 precipitation of poorly soluble hydroxides and hydroxycarbonates (Kirwin et al., 2013). As a

56 result, pH is reduced to below 9.0. Even so, drainage from seawater neutralized storage areas

57 has been shown to be high in Al, Mo, As, V and Ga (Department of Environment and

58 Heritage Protection, 2012). Treatment of drainage waters by conventional methods is likely

59 to be expensive, especially if it is to be continued for many decades after closure. A low-cost,

60 passive option, with green connotations, such as a constructed wetland, is an attractive

61 alternative.

62 Inorganic contaminants are sequestered within the wetland filter matrix by

63 adsorption/surface precipitation and bulk precipitation reactions (Westholm, 2006;

64 Gustafsson et al., 2008; Vymazal and Kropfelova, 2008; Haynes, 2014). Commonly used

65 filter materials in constructed wetlands are sands and gravels but these do not normally have

66 a high adsorption capacity so that the capacity of a wetland to remove inorganic contaminants

67 can decrease greatly over time and/or be highly variable (Haynes, 2014). Nevertheless, the

68 removal efficiency of wetlands for inorganic ions can be improved with the use of active

69 filter materials with reactive Fe/Al hydrous oxide adsorption surfaces (Genc-Fuhrman et al.,

70 2007; Gustafsson et al., 2008). The most commonly used materials are blast furnace slag,

71 steel slag and alum water treatment sludge (Vohla et al., 2011; Babatunde et al., 2009) but

72 other materials such as iron ore, bauxite and bauxite processing residue have also showed

73 promise (Haynes, 2014).

74 There is very little research on the use of constructed wetlands to treat alkaline

75 wastewater and so far work has been concerned with wastewater streams high in Ca^{2+} where

76 insoluble Ca compounds can precipitate in the wetland (Mayes et al., 2006). However, in

77 alkaline drainage from bauxite residues the main cation present is Na^+. This presents practical

78 problems since most Na compounds are highly soluble so that adsorption reactions onto the

79 surfaces of wetland filter media are potentially the major removal mechanism within a

80 wetland. The drainage can have a pH of 8.0-8.6 and contain concentrations of Al of < 20 mg

81 L^{-1}, those of Mo, Ga and V < 1.0 mg L^{-1} and As < 0.1mg L^{-1}. The purpose of this study is to

82 use batch adsorption studies to investigate materials with potential use as filter materials in

83 constructed wetlands for treatment of the drainage. Potential filter media, readily available in

84 the study area (bauxite residue sand, bauxite and alum water treatment sludge), were used as

85 adsorbent materials along with blast furnace slag for comparison (the most commonly used

86 waste adsorbent filter material) and the effects of pH, initial adsorbate ion concentration and

87 contact time on Mo, Ga, V and As adsorption were investigated.

88

2. Materials and Methods

89

90

91 2.1. Sample Description

92

93 Water treatment sludge was obtained from the Seqwater Mount Crosby Water Treatment

94 Plant (Brisbane), water-quenched BF slag was obtained from the BlueScope Steel Ltd., Port

95 Kembla Steelworks (New South Wales, Australia) and bauxite (from the Weipa deposit,

96 Queensland) and bauxite residue sand were sourced from Rio Tinto Alcan (Yarwun Alumina

97 Refinery). The residue sand was treated with acid (HCl) to give a pH of approximately 9.0

98 and then washed with distilled water. All samples were dried and ground (< 200 µm) prior to

99 use.

100   Elemental composition of materials was measured by inductively couple plasma atomic

101 emission spectrometry (ICP-AES) after digestion in a microwave system with HNO_3, HCl

102 and HF (CEM, 1993). Specific surface area of samples was determined by the BET/N_2

103 adsorption method, and zero point of charge (PZC) was determined using a Laser Zeta metre.

104 Materials were subjected to X-ray diffraction analysis to determine their mineralogy.

105 Effective cation exchange capacity, pH and electrical conductivity (EC) (1:5 material/water

106 ratio) were determined as described by Rayment and Higginson (1992). Cu, Zn, Cr, Cd, Pb

107 and As were extracted from wastes by the Toxicity Characteristic Leaching Procedure (TCLP)

108 (USEPA Method 1311; USEPA, 1992), and metals were measured by ICP-AES.

109

110 2.2. Aluminium precipitation

111 To determine the pH range over which Al would precipitate, an Al solution of 10 mg L^{-1} was

112 prepared in 0.01M NaCl using $AlCl_3$. A concentration of 10 mg Al L^{-1} was used as this is

113 within the range normally found in the drainage water. Aliquots (20 mL) were transferred to

114 50 mL centrifuge tubes and the pH adjusted from 3-12 using HNO_3 and NaOH. Once the pH

115 had stabilized the solutions were shaken for 2h. During that time, pH was checked and

116 readjusted if necessary every half hour. Resulting solutions were centrifuged (400 rpm for 10

117 min) and the filtered supernatant was analysed for Al by inductively coupled plasma atomic

118 emission spectrophotometry (ICP-AES). To determine if Al precipitation is affected by the

119 presence of a potential filter material, the above procedure was repeated but centrifuge tubes

120 also contained 200 mg of acid-washed silica sand. Experiments were carried out in triplicate.

121   To determine the potential cumulative effect of precipitated Al over the surfaces of a

122 filter material on adsorption of the other contaminant ions (Mo, V, As, Ga), solutions of 10 or

123 100mg L^{-1} Al (as $AlCl_3$) in 0.01 M NaCl were equilibrated with 200 mg of acid-washed silica

124 sand for a period of 2 h at a pH of 6.7 (a value derived from equilibration experiments

125 described below) by the procedures described above. The sand was subjected to 0, 10 or 20

126 equilibration cycles with Al solutions after which it was recovered from centrifuge tubes and

127 dried. Solutions of 1 mg L^{-1} Mo, V, As or Ga were prepared in 0.01 M NaCl using $MoNa_2O_4$,

128 NaO_3V, Na_2HAsO_4 and $Ga(NO_3)_3$. Samples of treated sand (200 mg), in triplicate, were

129 equilibrated with 20 mL of solution containing the target ion for 2 h on an end-over-end

130 shaker. At the beginning of the equilibration, and every half hour, pH was adjusted/readjusted

5

131 to pH 6.7 if necessary. The resulting solutions were centrifuged and ions in the filtered

132 solutions measured by ICP-AES.

133

134 2.3. Adsorption Experiments

135 Batch adsorption studies were performed to determine the extent of adsorption of each

136 individual ion at room temperature (25 °C). All experiments were carried out in triplicate at a

137 constant ionic strength provided by 0.01 NaCl. The effect of pH on Mo, V, As and Ga

138 adsorption was investigated over the pH range of 3 to 10 with an initial metal concentration

139 of 1 mg L^{-1} and adsorbent dosage of 10 g L^{-1}. The concentration of 1 mg L^{-1} in solution was

140 used for consistency and because it is above that of normal concentrations found in drainage

141 and therefore represents the maximum concentration that is likely to be needed to be removed

142 by adsorption (taking account that as the storage area dries out concentrations of contaminant

143 ions in drainage are likely to rise). Samples of waste material (200 mg) were weighed into

144 50-mL centrifuge tubes and 10 mL of 0.01 M NaCl was added. The mixture was shaken for 1

145 h and then adjusted to desired pH using HNO$_3$ or NaOH. Once the pH had stabilized, 10 mL

146 of an individual heavy metal solution (in 0.01 M NaCl and at twice the desired final metal

147 concentration) was added and the pH was adjusted again. The mixture was shaken on an end-

148 over-end shaker for 2 h. During this period, the pH was checked and readjusted, if necessary,

149 every half hour. The resulting solution was centrifuged (4,000 rpm for 10 min) and the

150 filtered supernatant was analysed for the appropriate aqueous heavy metal by ICP-AES.

151 Preliminary experiments showed that a 2-h contact time was adequate to reach an equilibrium.

152 The percentage of metal adsorbed was calculated from the difference between that added and

153 that remaining in solution.

154   To construct adsorption isotherms, ten different initial concentrations of Mo, V, As and

155 Ga (in 0.01 M NaCl) ranging from 1 to 320 mg L^{-1} were used (at pH 6.7 with an adsorbent

156 dosage of 10 g L^{-1}). Adsorption data (equilibrium metal concentration versus quantity

157 adsorbed) were fitted to the Langmuir and Freundlich equations (Apak, 2002). The effect of

158 contact time, varying from 10 to 300 min, was studied at pH 6.7, a dosage level of 10 mg L^{-1}

159 and an initial concentration of Mo, V, As and Ga of 1mg L^{-1}. The data was fitted to pseudo-

160 first-order and pseudo-second-order kinetic models.

161   In order to determine whether Al would be released from the adsorbents if they were

162 used as wetland filter material, samples of the four materials were equilibrated in 0.01 M

163 NaCl for 2 h at pH values of 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0 and 12.0 as described

164 above. Concentrations of Al in the centrifuged supernatants were measured by ICP-AES.

165

166 **3. Results and Discussion**

167

168 3.1. Properties of the Adsorbents Materials

169

170 The elemental content and mineralogical composition of the four adsorbent materials is

171 shown in Table 1. The bauxite used originated from the Weipa deposit, Cape York Peninsular,

172 northern Queensland (Loughnan and Bayliss, 1961) and its mineralogy was dominated by

173 gibbsite with some boehmite, quartz, kaolinite, hematite and goethite present (Table 1).

174 Consequently it had a very high Al content and a significant Fe and Si content (Table 1). It

175 had a pH of 7.3, and a surface area of 28.97 m^2 g^{-1} which is greater than that for BF slag or

176 residue sand (Table 2).

177   The main metallic element present in water treatment sludge was Al although some Fe

178 was also present (Table 1). It consisted of amorphous material although small amounts of

179 gehlenite ($Ca_2Al_2SiO_7$) were also present. Once alum dissolves in water, Al^{3+} exists in

180 aqueous solution as aluminohexahydronium ions $(Al \cdot 6H_2O)^{3+}$ and these dissociate

181 sequentially as pH increases to form species such as $[Al(H_2O)_5OH]^{2+}$. These species

7

182 polymerize to form positively charged polynuclear complexes which form a gel-like

183 substance that adsorbs and coagulates colloidal materials such as soluble organic matter and

184 fine soil particles from drinking water. The precipitated material exists as amorphous material

185 with a slightly acidic pH (6.4) and a very high surface area (47.17 m^2g^{-1}; Table 2) which

186 favours its use as an adsorbent.

187 The elemental content of residue sand was dominated by Fe and significant amounts of

188 Na, Si and Al were also present (Table 1). It had a pH of 9.1 and its mineralogy was

189 composed of hematite and sodalite with gibbsite being subdominant (Table 1). The surface

190 area of the red sand (17.13 $m^2\ g^{-1}$) was considerably smaller than that obtained for water

191 treatment sludge and bauxite (Table 2). The high pH/surface alkalinity of bauxite residue

192 favours both adsorption and precipitation of heavy metal cations (Zhou and Haynes, 2011a)

193 but the same properties are likely to hinder anion adsorption (Zhou and Haynes, 2012).

194 Blast furnace slag is produced during pig iron production when limestone flux is added

195 to the melt and fusible calcium silicate is formed which along with other impurities is poured

196 off. The slag used was water-quenched and the rapid cooling results in formation of a poorly

197 ordered, amorphous, glassy sand-like material. The high content of Si and Ca and significant

198 Mg and Al content reflects the slag composition which is predominantly amorphous Ca(Mg)

199 silicate with some gehlenite [$CaAl(AlSiO_7)$] (Table 1). The high pH of the slag (10.2) (Table

200 2) is due to the presence of Ca silicate which hydrolyses to release OH^- ions (Haynes et al.

201 2013). The slag had the lowest surface area (3.37 $m^2\ g^{-1}$) of the four materials used (Table 2).

202 For their use as filter materials, it is essential that materials are considered as non-toxic

203 wastes. The TCLP leaching values for all metals tested were extremely low and well below

204 regulatory guidelines for toxic wastes (Table 2) (USEPA, 1992). Thus, any of the materials

205 can be readily used as adsorbents/filter materials without the prospect of further

206 contaminating the wastewater with metals. Particularly for water treatment sludge and

207   bauxite, which are composed principally of Al, it is important that they do not contaminate

208   wastewater by release substantial quantities of Al. However, between the pH values of 6.0

209   and 8.0, concentrations of Al in equilibrium solutions with the materials were very low (<

210   0.15, 0.03, 0.13 and 1.35 mg L^{-1} for water treatment sludge, bauxite, blast furnace slag and

211   residue sand respectively) (data not shown). Some solubilization of Al was evident for all of

212   the materials at pH values of 4.0 and below and 9.0 and above.

213

214   3.2. Aluminium precipitation

215   As demonstrated in Fig 1, Al precipitates as hydroxyl-Al in the pH range 7-8 in aqueous

216   solution and 6-8.5 in the presence of silica sand in solution. At circumneutral pH, Al is

217   insoluble and precipitates as $Al(OH)_3$ but is soluble at low pH as Al^{3+}, $Al(OH)_2^+$ and

218    $Al(OH)_2^+$ and at high pH as $Al(OH)_4^-$ and $Al(OH)_5^{2-}$ (Frink and Peech, 1963). In leachates

219   from residue mud at a pH of about 8.0 -8.6 it will be present predominantly as $Al(OH)_4^-$ and

220   the pH needs to be reduced to below 8 to cause its precipitation. The presence of silica sand

221   (simulating the presence of a filter material in a wetland) helped activate precipitation

222   reactions by providing a surface for nucleation to occur.

223   Experiments where silica sand was equilibrated with Al solutions of 10 mg L^{-1} for up to

224   20 cycles failed to definitively demonstrate that Al-treated sand had a significant capacity to

225   adsorb Mo, V, As or Ga although there was some removal of Ga from solution (data not

226   presented). However, when a concentration of 100 mg Al L^{-1} was used (Fig 1), 10 and 20

227   cycles of Al-treatment resulted in the sand having a substantial adsorption capacity for the

228   target ions and for Mo, V and Ga, 20 cycles resulted in greater adsorption than 10 cycles. At

229   pH 6.7, Al will have precipitated as amorphous and crystalline $Al(OH)_3$ as a coating over the

230   sand particles forming highly active amphoteric adsorption surfaces (McBride 1982). From

231   the above results, it seems possible that the precipitation of Al on the surfaces of wetland

232   filter materials may, in the long-term, create new highly-active adsorption surfaces that will

233   adsorb the other contaminants ions. This aspect deserves further study particularly since, in

234   the long-term, any active filter material used will become saturated with adsorbent ions.

235   Untreated sand had an apparent ability to adsorb Ga since initial concentrations of 1 mg

236   L^{-1} were reduced to 0.21 mg L^{-1} and Al-treatment of the sand further reduced equilibrium Ga

237   concentrations (Fig. 1). However, at pH 6.7 Ga tends to precipitate as insoluble $Ga(OH)_3$ and

238   the presence of sand particles provided a surface for nucleation to take place. Similarly,

239   Music and Wolf (1979) concluded that at pH values of 6.0-7.0 Ga was present predominantly

240   as insoluble $Ga(OH)_3$. Thus, removal of Ga at pH 6.7 is as a result of both precipitation and

241   adsorption. Such results suggest that decreasing the pH of the drainage water down to about

242   7.0 would result in removal of most of the soluble Al and much of the Ga through

243   precipitation of insoluble metal hydroxide precipitates.

244

245   3.3. Effect of pH on adsorption

246   The main mechanism by which contaminant cations and anions are held on the surfaces of

247   active filter materials is by specific adsorption (chemisorption) which involves exchange of

248   ions with surface ligands on the variable charge surfaces of metal oxides/silicates and the

249   subsequent formation of covalent bonds with lattice ions on the surface. Beyond a certain

250   level of adsorption surface precipitation also occurs (McBride, 2000). As pH increases, the

251   surface charge on adsorption surfaces becomes increasingly negative resulting in greater

252   electrostatic repulsion between anions and the adsorbent surface thus disfavouring adsorption.

253   Above the PZC (5.6, 5.8, 6.6 and 7.9 for water treatment sludge, BF slag, red sand and

254   bauxite respectively) surfaces carry a net negative charge. Nonetheless, as pH is raised,

255   hydrolysis of anions occurs and this also greatly affects adsorption since specific adsorption

256   is favoured at pH values close to the acid dissociation constants (pK_a) (Bowden et al., 1980).

257   The interaction between these two factors determines the shape of the adsorption

258   envelopes for the oxyanions (Fig. 2). For arsenic acid (H_3AsO_4) the pK_1 and pK_2 are at 2.2

259   and 6.8 respectively. As a result, between 2.2 and 6.8 As(V) is already present predominantly

260   as $H_2AsO_4^-$ but the proportion of the more strongly adsorbed $HAsO_4^{2-}$ is increasing

261   (Goldberg, 2002; Zhou and Haynes, 2012). With increasing pH above 6.8 electrostatic

262   repulsion results in a pronounced decrease in As adsorption. Similarly, in dilute solutions the

263   dominant species of V are the oxyanions $VO_2(OH)_2^-$ and $VO_3(OH)^{2-}$ since the pK_1 and pK_2

264   for H_3VO_4 are at pH 3.5 and 7.8 (Crans et al., 2004). Adsorption is at a maximum between

265   pH 3.0 and 6.0-8.0 (Fig. 2). Above these values there is a characteristically rapid decline in

266   adsorption due to electrostatic repulsion as the proportion of VO_4^{3-} increases (Peacock and

267   Shermann, 2004; Naeem et al., 2007). For Mo the pK_1 and pK_2 for H_2MoO_4 are close

268   together at pH 3.6 and 4.0 and MoO_4^{2-} is the dominant species normally present. As a result,

269   adsorption decreased above pH 4.0 for residue sand and BF slag and was insignificant above

270   pH 7.0. This is a similar pattern to that which occurs for Fe and Al oxides (Goldberg et al.,

271   1996; Kim and Jang, 2010). However, for water treatment sludge and bauxite maximum

272   adsorption extended to pH 6.0 and adsorption was still appreciable at pH 7.0. This is an

273   adsorption envelope more typical for clay minerals (Goldberg et al., 1996).

274   The chemistry of Ga(III) is much less well known than that for the other three adsorbates.

275   However, in aqueous solutions Ga(III) exists at pH 1 as Ga^{3+}, at pH 3 mainly as $Ga(OH)^{2+}$, at

276   pH 4.0 predominantly as $Ga(OH)_2^+$ and at pH 7.0 it is in the form of insoluble $Ga(OH)_3$

277   (Music and Wolf, 1979). Thus, at low pH (< pH 3.0) there is electrostatic repulsion between

278   Ga^{3+} and the positively charged surfaces which hinders adsorption (Music and Wolf 1979;

279   Fig. 2). Ga is specifically adsorbed as the $Ga(OH)^{2+}$ and $Ga(OH)_2^+$ cations so that adsorption

280   is at a maximum at pH values of 3.0-4.0. The adsorbed $Ga(OH)_2^+$ transforms to insoluble

281    $Al(OH)_3$ as pH rises and remains on the adsorbent surfaces. The $Ga(OH)_3$ is soluble in

282   alkaline solutions (> pH 7.0) and dissolves to form negatively charged gallate $[Ga(OH)_4^-]$. As

283   a result of electrostatic repulsion between the gallate and the negatively charged adsorbent

284   surfaces, adsorption declines rapidly above pH 7.0-8.0 (Fig. 2) (Music and Wolf, 1979;

285   Pokrovsky et al., 2004)

286   Water treatment sludge and bauxite had a superior ability to retain V, As and Mo at

287   higher pH values than residue sand and BF slag (Fig. 2). A contributing factor to this is that

288   both blast furnace slag and bauxite residue possess substantial residual alkalinity so that their

289   surface pH is likely to be significantly higher than that of the equilibrium solution (Zhou and

290   Haynes, 2011a). This would inhibit adsorption of the target ions at higher measured

291   equilibrium pH values. In relation to the optimum pH for simultaneous adsorption of all four

292   ions from alkaline solutions, it is Mo which is limiting since, as noted above, adsorption

293   declined above pH 6.0 even for water treatment sludge and bauxite. However in the range of

294   6.0-7.0 adsorption of Mo was still substantial and therefore for further studies a pH of 6.7

295   was chosen.

296   The above results suggest that the pH of the drainage water will need to be lowered

297   from above 8.0 into the range of 6.0-7.0 for effective removal of the target metals. Biological

298   activity is the key to pH reduction in wetlands. That is, the presence of macrophyte root

299   systems permeating through the filter bed, and the associated intense microbial activity in the

300   rhizosphere, results in high production of CO_2 which dissolves in water to produce carbonic

301   acid (Mayes et al., 2006, 2009). Other passive methods of acidification include use of a

302   separate wetland with an organic matter filter material to greatly stimulate microbial activity

303   and buffer pH (Courtney, 2013) and the use of acidic peat filters (Mayes et al., 2009). In

304   addition, water treatment sludge has a pH of 6.4 although whether it could buffer the alkaline

305   drainage to this pH for prolonged periods is, as yet, unknown.

306

307 3.4. Adsorption Isotherms

308

309 Both the Freundlich and Langmuir models are commonly used to empirically describe

310 adsorption isotherms for ions onto adsorbent materials (Apak, 2002) and frequently both

311 models describe adsorption adequately (Al-Degs et al., 2006; Naeem et al., 2007). The

312 Langmuir equation is based on monolayer adsorption on active sites of the adsorbent:

313 $$q_e = b q_{max} C_e / (1 + b C_e) \qquad (5)$$

314 where q_e and C_e are equilibrium concentrations of metal in the adsorbed (mg g^{-1}) and liquid

315 phases (mg L^{-1}), respectively. q_{max} and b are the Langmuir constants which are related to the

316 maximum adsorption capacity and energy of adsorption, respectively.

317 On the other hand, the Freundlich isotherm explains adsorption onto a heterogeneous surface

318 with uniform energy:

319 $$q_e = K_f C_e^{\frac{1}{n}} \qquad (7)$$

320 where q_e and C_e are the equilibrium concentrations of metal in the adsorbed (mg g^{-1}) and

321 liquid phases (mg L^{-1}), respectively. K_f and n are the Freundlich constants which are related

322 to adsorption capacity and intensity, respectively. In general, adsorption data for V and As

323 onto the four adsorbents fitted equally well to the Freundlich and Langmuir models but for

324 Mo and Ga the Freundlich equation generally gave higher R^2 values (Table 3).

325 For the Freundlich model, values of n for Mo, V and As ranged from 1.24 to 3.26

326 (Table 3). Values of n >1 indicate that bonding energies decrease with increasing surface

327 adsorption densities in accordance with preferential adsorption occupying surface sites in the

328 order from strongest to weakest binding strength (Apak, 2002). In addition, n >2 (as was the

329 case for water treatment sludge and bauxite for Mo, V and As) has be interpreted by some as

330 an indication of an adsorbent with good adsorbent characteristics for the solute being

13

331 considered (Treybal, 1980). The relatively low values of n for Ga adsorption particularly for

332 slag and residue sand reflect almost linear adsorption (that is, a value of 1 indicates linear

333 adsorption; see Fig. 3) suggesting precipitation reactions may well be occurring (Bradl, 2004).

334 As noted earlier, precipitation of $Ga(OH)_3$ at pH 6.7 is likely.

335   For all four ions tested, values for q_{max} were greatest for water treatment sludge and a

336 similar trend was evident for the Freundlich K_f factor. This supports the outcomes of earlier

337 work which showed that because of its amorphous nature, and large surface area, alum water

338 treatment sludge is an extremely effective adsorbent for ions such as Cd(II), Cu(II), Pb(II),

339 Zn(II), Cr(III), Cr(VI) As(II), As(V), Se(IV) and Se(VI) (Zhou and Haynes, 2011a,b; 2012).

340 Bauxite was also an effective adsorbent particularly for Mo, V, and Ga (Fig. 2) and generally

341 more effective than the other two materials examined.

342

343

344 3.5. Effect of Contact Time
345

346   Figure 3 shows the adsorption of metals onto four waste materials as a function of contact

347 time. Adsorption onto all the materials occurred very rapidly and was complete after 60-90

348 min. In order to evaluate adsorption kinetics, pseudo-first-order and pseudo-second-order

349 models were employed to interpret the experimental data. The pseudo-first-order equation

350 can be represented by:

351 $$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (9)$$

352 where k_1 (min^{-1}) is the pseudo-first-order adsorption rate constant, q_t is the amount adsorbed

353 at time t (min) and q_e denotes the amount adsorbed at equilibrium, both in millgrams per

354 gram. The pseudo-second-order equation can be expressed as:

355 $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (10)$$

356 where k_2 [g (mg min)$^{-1}$] is the adsorption rate constant of pseudo-second order.

357 Based on the obtained correlation coefficients, the pseudo-second-order equation gave a

358 better fit to the experimental kinetic data than the pseudo-first-order model and calculated

359 pseudo-second-order q_e values were in good agreement with the experimental values (Table

360 3). This suggests that chemisorption rather than diffusion/ion exchange was the rate-limiting

361 step to adsorption (Ho and McKay, 1999). Indeed, the oxyanions arsenate, molybdate and

362 vanadate are all known to form strong inner sphere monodentate and bidentate complexes

363 with Fe and Al oxide surfaces (Sparks, 2003). Although, as already noted, Ga may be

364 precipitating as $Ga(OH)_3$ at pH 6.7, it is also known to be specifically adsorbed in both the

365 $Ga(OH)^{2+}$ and $Ga(OH)_2^+$ forms (Lin et al., 1997; Pokrovsky et al., 2004).

4. Conclusions

367 Results presented here demonstrate that reduction in solution pH will be the critical factor

368 determining the effective use of constructed wetlands to remove Al, Mo, Ga, V and As from

369 alkaline (pH 8.0-8.6) drainage water. Decreasing pH to below 7.0 will result in precipitation

370 of Al as $Al(OH)_3$ and a substantial portion of Ga as $Ga(OH)_3$ as well as promoting surface

371 adsorption of Mo. Water treatment sludge has a pH of 6.4 so that it may buffer the pH to a

372 value low enough for ion removal without pH adjustment while biological acidification

373 within a wetland, through carbonic acid production, will also tend to lower pH.

374 This study is the first step in developing constructed wetland technology for use in

375 treatment of wastewater from bauxite residue storage areas. The next stage is to examine the

376 effect of particle size (sand-sized particles as used as wetland filter material versus ground

377 material as used here) and ionic strength (0.3 M Na as present in drainage water versus

378 0.01M as used here) on removal of Mo, As, V and Ga by water treatment sludge and bauxite

379 (the two most promising materials) in batch and column studies.

380

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486   regeneration. Water Air Soil Pollut. 223, 5563-5573.

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496 **Figure Captions**

497

498 **Fig. 1-** (a) Effect of solution pH on the solubility of Al (at 10 mg L^{-1}) either in aqueous

499 solution (control) or in the presence of silica sand (sand) and (b) effect of equilibration of

500 silica sand with an 100 mg L^{-1} Al solution for 0, 1, 10 or 20 cycles at a pH of 6.7 on amounts

501 of Mo, V, As or Ga remaining after equilibration of 1 mg L^{-1} solutions with the sand samples

502 for 2 h. Standard errors of the mean shown.

503

504 **Fig. 2-** Influence of solution pH on the relative adsorption (% of added ion) of (a) Mo, (b) V,

505 (c) As and (d) Ga onto alum water treatment sludge (WT sludge), bauxite, blast furnace slag

506 (BF slag) and bauxite residue sand. Standard errors of the mean shown.

507

508 **Fig. 3-** Effect of equilibrium metal concentration on the quantity of (a) Mo, (b) V, (c) As and

509 (d) Ga adsorbed onto alum water treatment sludge (WT sludge), bauxite, blast furnace slag

510 (BF slag) and bauxite residue sand. Standard errors of the mean shown.

511

512 **Fig. 4-** Effect of contact time on the relative adsorption (% of added ion) of (a) Mo, (b) V, (c)

513 As and (d) Ga onto alum water treatment sludge (WT sludge), bauxite, blast furnace slag (BF

514 slag) and bauxite residue sand. Standard errors of the mean shown.

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Table 1 Elemental and mineralogical composition of the waste materials

Material	Elemental composition (g kg^{-1})								Mineralogical composition
	Si	Fe	Al	Ca	Mg	K	Na	P	
WT sludge	24.9	18.4	111.1	0.081	0.091	0.454	0.433	0.864	Dominant: poorly crystalline amorphous material Minor: gehlenite
Bauxite	18.3	33.4	132.2	0.11	0.21	0.31	0.26	0.63	Dominant: gibbsite Sub-dominant: boemite, quartz kaolinite, anatase, hematite
BF slag	110.2	1.08	5.93	63.9	4.855	1.886	1.619		Dominant: amorphous glass Minor: gehlenite
Residue sand	51.9	130.3	46.9	6.12	0.102	0.209	64.7	0.581	Co-dominant: hematite, sodalite; Sub-dominant: gibbsite Minor: anatase, calcite, goethite

Table 2 TCLP – extractable metals and some chemical properties of the waste material

Material	Chemical properties					TCLP – extractable metals (mg L^{-1})				
	pH	EC (S m^{-1})	PZC (pH)	CEC (cmol$_c$ kg^{-1})	S$_{BET}$ (m^2 g^{-1})	Cu	Zn	Cr	Cd	Pb
WT sludge	6.4	40.1	5.6	6.78	47.17	0.03	0.01	0.03	0.005	0.016
Bauxite	7.3	2.24	7.9	4.32	28.97	0.039	0.01	0.018	0.005	0.003
BF slag	10.2	11.9	5.8	1.18	3.37	0.026	0.015	0.074	0.008	0.003
Residue sand	9.1	29.3	6.6	5.88	17.13	0.028	0.014	0.002	0.003	0.015
Regulatory level						ns	ns	5.0	1.0	5.0

Table 3 Langmuir and Freundlich isotherm constants and Correlation coefficient (R^2) for adsorption of Mo(VI), V(V), As(V) and Ga(III)   onto four waste materials.

Metal	Adsorbent	Langmuir isotherm			Freundlich isotherm		
		q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_f	n	R^2
Mo(VI)	WT sludge	9.53	0.04	0.96	0.72	2.04	0.98
	Bauxite	2.19	0.08	0.95	0.37	2.83	0.99
	BF slag	0.08	5.62	0.96	0.64	1.24	0.96
	Residue sand	0.17	0.13	0.79	0.02	1.42	0.97
V(V)	WT sludge	13.02	0.26	0.99	2.12	2.22	0.93
	Bauxite	3.62	0.10	0.98	0.71	3.26	0.99
	BF slag	4.23	0.01	0.97	0.04	1.24	0.99
	Residue sand	4.33	0.02	0.89	0.13	1.55	0.99
As(V)	WT sludge	17.36	0.31	0.99	3.06	2.39	0.89
	Bauxite	2.95	0.07	0.9	0.62	3.20	0.95
	BF slag	1.27	0.06	0.95	0.12	1.68	0.96
	Residue sand	10.36	0.03	0.89	0.68	2.07	0.99
Ga(III)	WT sludge	28.74	0.60	0.89	10.24	1.34	0.94
	Bauxite	19.72	0.88	0.92	4.32	1.13	0.95
	BF slag	3.21	5.40	0.93	0.62	0.89	0.95
	Residue sand	8.70	1.99	0.91	2.45	0.85	0.97

Table 4 Pseudo-first-order and pseudo-second-order rate constants, experimental q_e values and correlation coefficients (R^2) for adsorption of Mo(VI), V(V), As(V) and Ga(III) onto four waste materials.

| Material	Metal	Pseudo-first order				Pseudo-second order			
		q_e (g g^{-1})		k_1 (min^{-1})	R^2	q_e (g g^{-1})		k_2 (g g^{-1} min^{-1})	R^2
		Experimental	Calculated			Experimental	Calculated		
WT sludge	Mo(VI)	0.098	0.011	0.017	0.94	0.098	0.098	4.320	0.99
	V(V)	0.099	0.002	0.024	0.95	0.099	0.099	46.184	0.99
	As(V)	0.091	0.004	0.016	0.86	0.091	0.092	11.755	0.99
	Ga(III)	0.089	0.001	0.005	0.42	0.089	0.088	54.637	0.99
Bauxite	Mo(VI)	0.099	0.002	0.013	0.90	0.099	0.099	22.914	0.99
	V(V)	0.099	0.002	0.020	0.86	0.099	0.099	30.421	0.99
	As(V)	0.091	0.005	0.019	0.91	0.091	0.092	11.545	0.99
	Ga(III)	0.091	0.001	0.013	0.69	0.091	0.091	48.411	0.99
BF slag	Mo(VI)	0.019	0.010	0.022	0.94	0.019	0.020	4.497	0.99
	V(V)	0.089	0.012	0.018	0.95	0.089	0.090	9.674	0.99
	As(V)	0.067	0.014	0.020	0.97	0.067	0.068	3.901	0.99
	Ga(III)	0.096	0.019	0.026	0.94	0.096	0.097	3.545	0.99
Residue sand	Mo(VI)	0.011	0.011	0.029	0.95	0.011	0.012	3.505	0.99
	V(V)	0.036	0.011	0.030	0.88	0.036	0.036	7.096	0.99
	As(V)	0.073	0.026	0.027	0.94	0.073	0.074	2.483	0.99
	Ga(III)	0.086	0.016	0.024	0.88	0.086	0.087	3.545	0.99

(a)

(b)
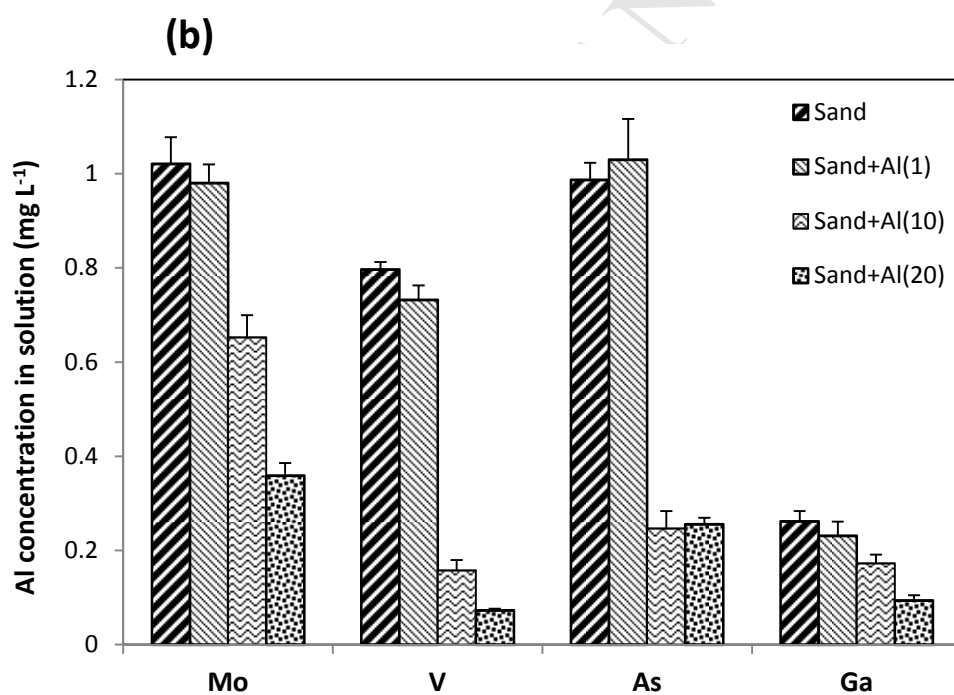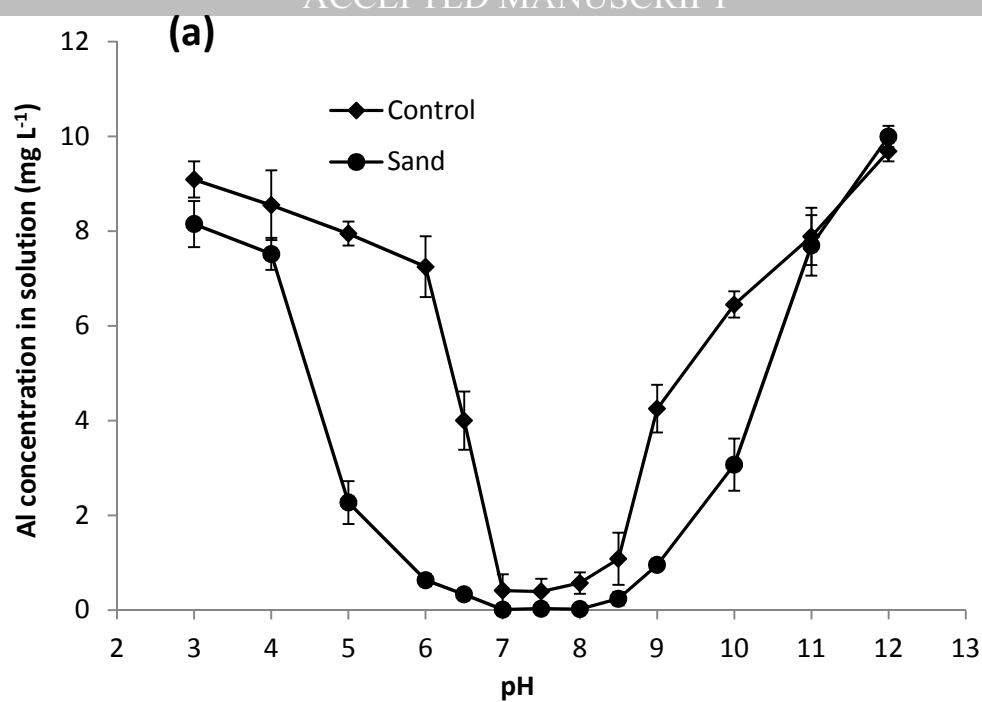
Fig. 1- (a) Effect of solution pH on the solubility of Al (at 10 mg L^{-1}) either in aqueous solution (control) or in the presence of silica sand (sand) and (b) effect of equilibration of silica sand with an 100 mg L^{-1} Al solution for 0, 1, 10 or 20 cycles at a pH of 6.7 on amounts of Mo, V, As or Ga remaining after equilibration of 1 mg L^{-1} solutions with the sand samples for 2 h. Standard errors of the mean shown.
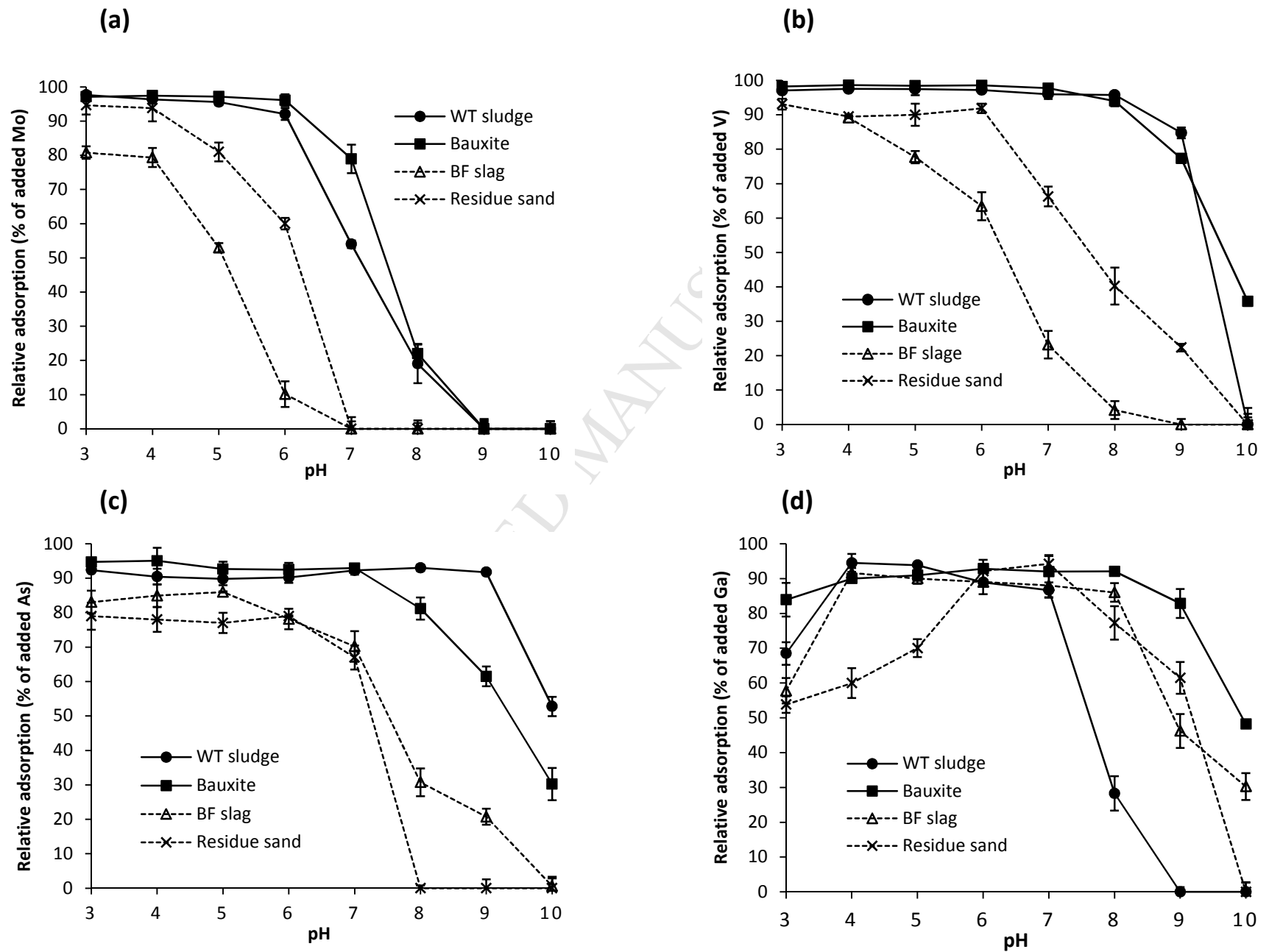
Fig. 2- Influence of solution pH on the relative adsorption (% of added ion) of (a) Mo, (b) V, (c) As and (d) Ga onto alum water treatment sludge

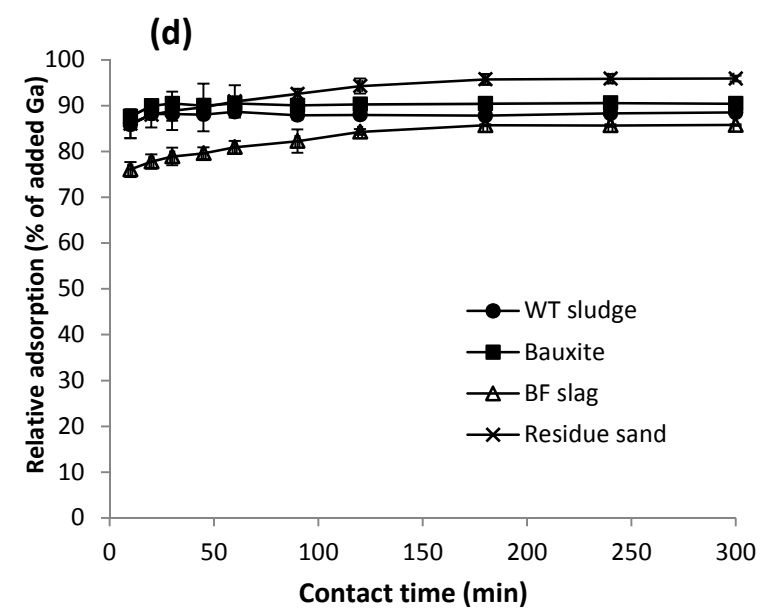(WT sludge), bauxite, blast furnace slag (BF slag) and bauxite residue sand. Standard errors of the mean shown.
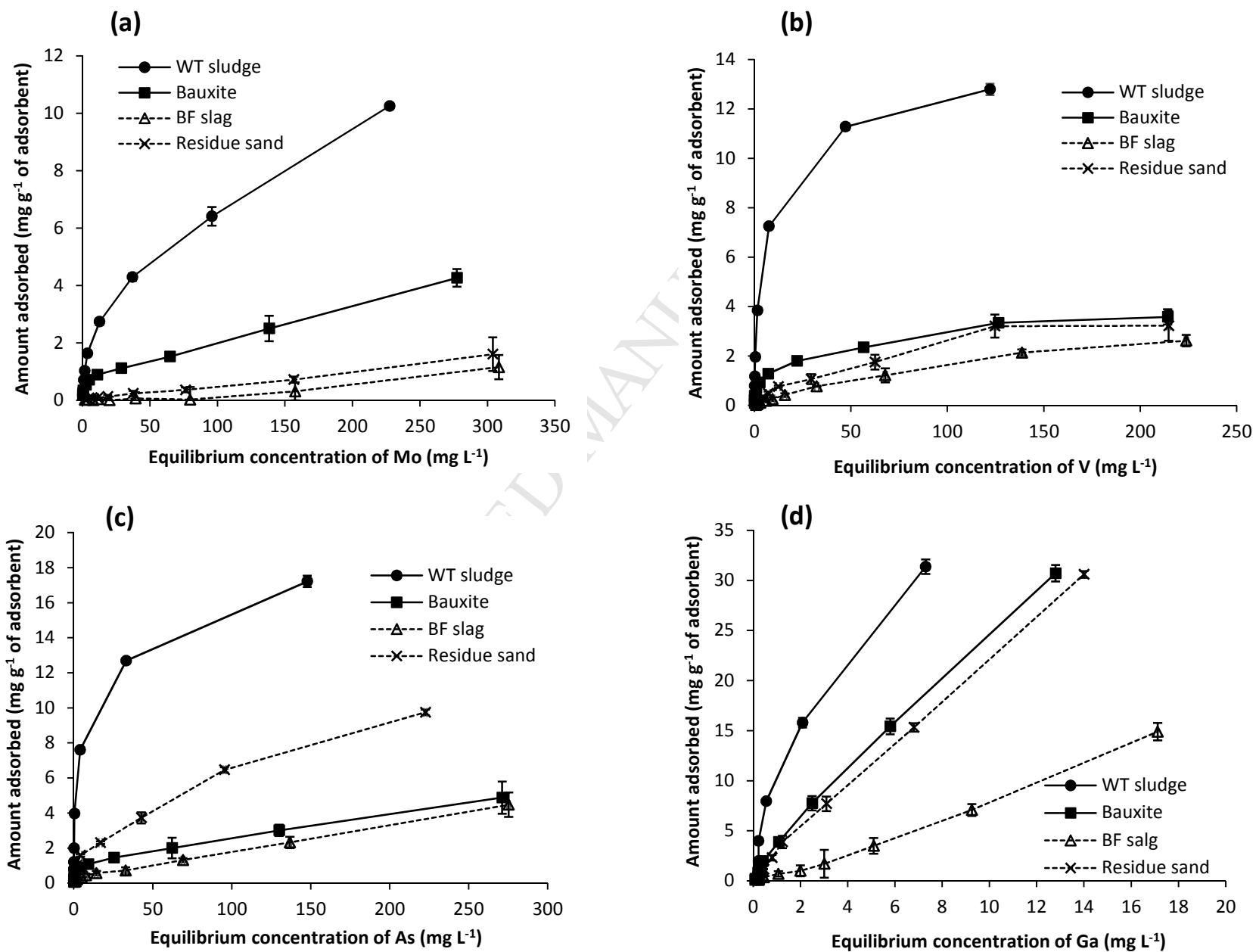
Fig. 3- Effect of equilibrium metal concentration on the quantity of (a) Mo, (b) V, (c) As and (d) Ga adsorbed onto alum water treatment sludge (WT sludge), bauxite, blast furnace slag (BF slag) and bauxite residue sand. Standard errors of the mean shown.
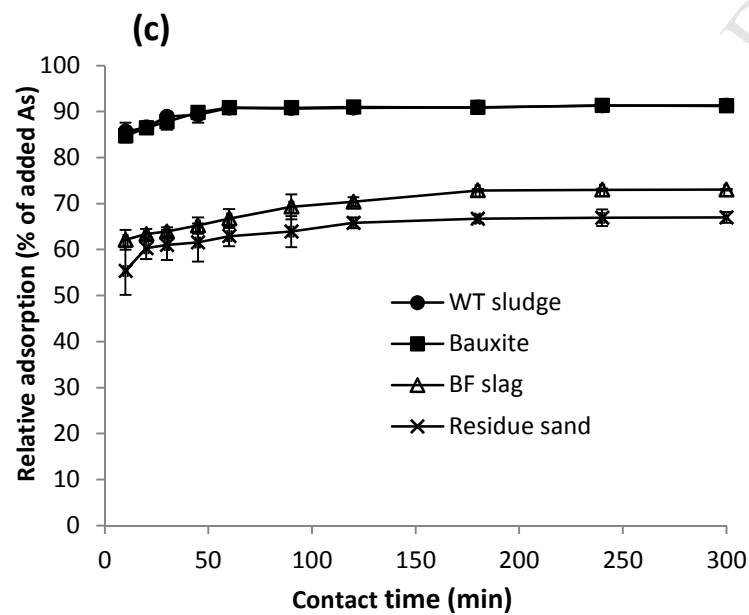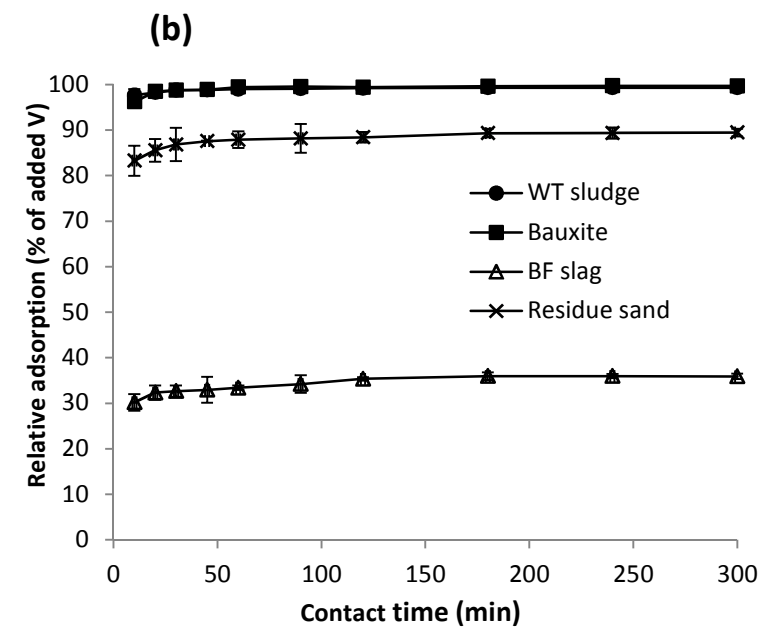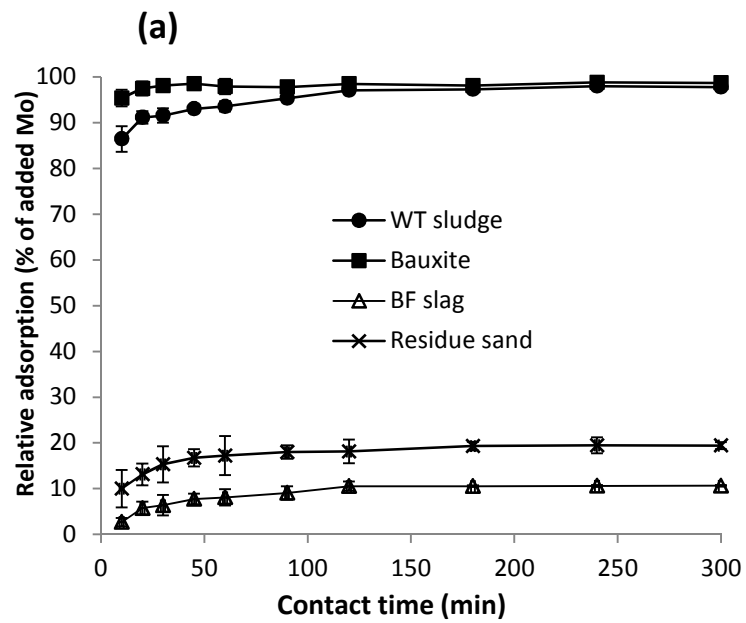
Fig. 4- Effect of contact time on the relative adsorption (% of added ion) of (a) Mo, (b) V, (c) As and (d) Ga onto alum water treatment sludge (WT sludge), bauxite, blast furnace slag (BF slag) and bauxite residue sand. Standard errors of the mean shown.

Highlights

- We study removal of Al, Ga, Mo, V, As from alkaline drainage using active filter media

- Al and to a lesser extent Ga precipitated out when pH was reduced to below 7.0

- Mo, As, V and Ga were adsorbed to the surfaces of filter materials below pH 7.0

- Water treatment sludge and bauxite were the most effective filter materials