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1
2 **Removal of glyphosate from aqueous environment by adsorption**
3 **using water industrial residual**

4
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14
15 **ABSTRACT:** This study investigated the glyphosate adsorption by water treatment residual
16 (termed as alum sludge) in dewatered form (DAS) and liquid form (LAS). Batch adsorption
17 tests were carried out with DAS at different pH, particle size and DAS mass. Standard jar tests
18 were conducted with LAS at two different concentrations (3 g/l and 5 g/l) for glyphosate
19 adsorption. Thereafter, the glyphosate-enriched LAS (after adsorption tests) was subjected to
20 sludge conditioning procedure with polymer LT25 as conditioner to explore any possible
21 further glyphosate reduction. The results indicate that alum sludge has the high adsorption
22 capacity of 85.9 mg/g for DAS and 113.6 mg/g for LAS. This demonstrated the potential of
23 the alum sludge to be an efficient and cost-effective adsorbent for glyphosate removal in
24 comparison with other adsorbents, such as soils, humic substances, clay minerals, and layered
25 double hydroxides (LDH). The polymer conditioning of the glyphosate-enriched LAS cannot
26 bring about the further glyphosate reduction in the supernatant of the dewatered LAS. Overall,
27 this study promotes the beneficial reuse of alum sludge in wide range of pollutant control in
28 environmental engineering.

29
30 **Keywords:** adsorption, adsorption isotherm, alum sludge, glyphosate, reuse, water treatment
31 residual

33 **1. Introduction**

34 Glyphosate (N-(phosphonomethyl) glycine) is one of the most widely applied broad-
35 spectrum herbicides in both agricultural and non-agricultural areas all over the world.
36 Introduced by Monsanto (an US chemical company) in early 1970s, it is now representing
37 60% of the global ‘broad-spectrum’ herbicide sales with the total global use of over 70,000
38 tonnes technical acid p.a. [1, 2].

39 Due to the vast quantities of glyphosate used, there are increased concerns of its impacts on
40 the environment, in which the glyphosate was entered via various routes during its
41 manufacture, use and runoff after use etc. [3-5]. Many cases of its poisoning in humans, with
42 a variety of symptoms including eye and skin irritation, contact dermatitis, eczema, cardiac
43 and respiratory problems and allergic reactions, increased the concern of its health impacts. A
44 comprehensive review of the acute toxic effects of glyphosate in humans can be found in
45 [Buffin and Topsy \[2\]](#). More recently, four different Roundup formulations of the herbicide
46 glyphosate manufactured by Monsanto were found highly toxic to human cells at
47 concentrations far below the recommended agricultural use levels [6, 7].

48 Regarding the residual of glyphosate in drinking water, there is still no guideline value, but
49 the EU limit for any herbicide in drinking water is 0.1 µg/l [8], which is a substitute for zero
50 in drinking water. Obviously, this is a big challenge for potable water treatment plant.
51 Considering the increasing reports about the occurrence of glyphosate in the aqueous
52 environment [9-12], it is reported that, in relation to the removal of the pesticides from
53 drinking water, it is estimated that the cost of installing the necessary facilities may be £1.0bn
54 with annual running costs being £50 - £100 m in the UK. Hence, the water pollution caused
55 by glyphosate must be under substantial control. Although a range of conventional methods
56 can be applied to remove glyphosate, which include activated-carbon, oxidation, ozonation
57 and photocatalytic degradation etc. [13-15], an efficient and cost-effective method is still
58 desirable. From the structural formula of glyphosate, it is known that the glyphosate is a kind
59 of organic phosphate in nature. Fortunately, it has been demonstrated especially in the recent
60 years that an inevitable water industrial residual in terms of alum sludge, can be reused as a

61 low-cost adsorbent for some pollutants immobilization. For example, alum sludge has been
62 examined extensively to exhibit excellent phosphorus (P) adsorption ability [16-21]. Alum
63 sludge is an inevitable by-product produced from water treatment plants worldwide when
64 aluminium sulphate, a most widely adopted water purification coagulant, is used as primary
65 coagulant to flocculate the source waters. The most recognised feature of alum sludge lies in
66 its local, easy and large availability. For example, in Ireland, 18,000 tonnes dry solids of alum
67 sludge in an annual basis is generated with landfill disposal costs of about €3.2 million. In the
68 UK, about 182,000 tonnes dry solids of waterworks sludge is generated each year, with
69 predominant disposal route to landfill as a “waste” with little known knowledge of reuse [22].
70 The research in University College Dublin, Ireland has been focused on identifying the
71 characteristics and the phosphorus adsorption capacity of the local alum sludge in Dublin [23-
72 26]. More significantly, a so-called alum sludge-based novel constructed wetland system has
73 been developed, which employed dewatered alum sludge as main substrate in treatment
74 wetland to enhance the phosphorus immobilization [27]. Therefore, it is assumed that the
75 alum sludge may have the potential as an efficient and low-cost adsorbent to extract
76 glyphosate from aqueous environment.

77 Thus, the aim of this study is to justify the feasibility of the alum sludge for glyphosate
78 immobilization. This will, of course, promote the beneficial reuse of alum sludge in wide
79 range of pollutant control in environmental engineering. Alum sludge in the forms of
80 dewatered alum sludge (DAS) cake and liquid alum sludge (LAS) has been used for
81 glyphosate adsorption tests. Firstly, batch tests were carried out to investigate the factors that
82 affect the glyphosate adsorption onto alum sludge and provide information, such as
83 equilibrium time and suitable initial glyphosate concentration range for the ensuing
84 equilibrium studies. Secondly, the adsorption equilibrium studies with different adsorption
85 isotherm models were conducted to determine the maximum adsorption capacity. Adsorption
86 kinetics of the glyphosate onto alum sludge was also studied. In addition, polymer
87 conditioning of glyphosate saturated LAS (after adsorption tests) was implemented with
88 Magnafloc LT25 for the purposes of sufficient solid-liquid separation and exploring any
89 possible further glyphosate reduction during the sludge conditioning.

2. Materials and methods

2.1. Alum sludge and glyphosate aqueous solutions

Two types of alum sludge were used in this study. DAS cakes were collected from the dewatering unit of the Ballymore-Eustace Water Treatment Plant, Co. Dublin, Ireland. LAS was collected from the influent of the thickening tank of the same water treatment plant. The nature of the plant and the characteristics of the alum sludge have been investigated and reported in our previous study [26]. After collection, the DAS was air dried at room temperature for some period resulting in an average moisture content of 23.4-23.7%. The DAS was then ground into different particle sizes (<0.063, 0.15-0.212, 0.425-0.6 and 1-2 mm). The LAS was concentrated to 3 g/l and 5 g/l, respectively, by settling and rejecting the supernatant. A 1,000 mg/l glyphosate stock solution was made up from Roundup[®] Pro Biactive[®], a commercial product which contains 360 g/l glyphosate. The stock solution was then diluted with distilled water to prepare the glyphosate solutions in various concentrations (0.5-500 mg/l) with the natural pH of 5.2-5.6 for testing. All the glyphosate solutions were well mixed and the concentrations were checked through P measurement based on the P content in glyphosate with the formula of C₃H₈NO₅P before use to ensure full solubilization of glyphosate in water. It should be noted such concentration range is unrealistic in natural aquatic system (highest concentration 328 µg/l [12]), but closer to the wastewater produced in glyphosate manufacturing (glyphosate content 2-3% [28]).

2.2. Batch test with DAS

Batch tests of glyphosate adsorption were carried out with the DAS at room temperature (22 °C) and initial glyphosate concentration of 50 mg/l. 10 ml of glyphosate stock solution and 190 ml of distilled water were added respectively to a series of 200 ml bottles with varied DAS mass. It was followed by the adsorption tests at 300 rpm on an orbital shaker (SSL1, Bibby Sterilin LTD, UK). The adsorption of glyphosate onto DAS was determined as a function of time, pH, particle size and alum sludge mass. To determine the pH effect on the adsorption of glyphosate, initial pH value was adjusted to 4.3, 5.6, 7.0 and 9.0, respectively, by adding 0.1 mol/l sulphuric acid and 0.1 mol/l sodium hydroxide, while the particle size and the alum sludge mass were fixed at <0.063 mm and 5 g/l, respectively. Adsorption test conducted as a function of particle size (<0.063mm, 0.150-0.212mm, 0.425-0.6mm and 1-2

121 mm) was performed at pH 5.6 and alum sludge mass of 5 g/l. Accordingly, the effect of alum
122 sludge mass on glyphosate adsorption was studied at particle size of <0.063 mm and pH 5.6
123 with different alum sludge mass of 0.5, 1, 3 and 5 g/l, respectively.

125 2.3. Jar test with LAS

126 Standard jar tests were performed to investigate the glyphosate adsorption rate by LAS at two
127 concentrations of 3 g/l and 5 g/l, respectively with mixed sludge samples of 500 ml in a series
128 of 1,000 ml beakers. At the beginning, initial glyphosate concentration of 10-50 mg/l (the
129 same with the DAS experiments) was adopted. But the equilibrium glyphosate concentrations
130 in the liquid were near the detective limit of the monitoring method and the residual
131 concentrations were difficult to be distinguished with the different initial concentrations.
132 Hence, the initial glyphosate concentrations were increased and finally the range of 200-500
133 mg/l was found to be suitable for the LAS tests. The jar tests were conducted under the room
134 temperature (22 °C) and the natural pH (5.2-5.6) of the glyphosate aqueous solution. A
135 common jar-stirring device of Triton - WRC type 131 was used to mix the sludge samples at
136 85 rpm for 24 hrs to allow the adsorption equilibrium to be reached. Thereafter, a standard
137 sludge conditioning procedure was applied with organic polymer of Magnafloc LT25 (Ciba
138 Speciality Chemicals Corporation) as conditioner in order to separate the glyphosate-enriched
139 sludge from the aqueous environment. During sludge conditioning, 100ml samples of the
140 stabilized sludge (with initial glyphosate 500 mg/l being added for adsorption trial) were
141 taken and placed into a series of 500 ml beakers. A wide range of polymer concentration (1, 5,
142 10, 20, 30, 40, 50 and 60 mg/l) was added to the sludge beakers. The beakers were then made
143 up to the 250 ml with distilled water to eliminate the volume effect of polymer addition, this
144 leads to the LAS concentrations of 1.2 g/l and 2 g/l with the initial values of 3 g/l and 5 g/l,
145 respectively, due to the dilution. The sludge samples were then mixed immediately to
146 promote the coagulation for 10 s at 100 rpm. Thereafter, the samples were subjected to a slow
147 mixture to enhance the flocculation for 60 s at 20 rpm. Settlement of the sludge samples was
148 allowed for 1 minute after conditioning and turbidity and suspended solid (SS) of the
149 supernatant were measured to determine the optimal dosage of the polymer. Glyphosate was
150 also determined to investigate whether there is further reduction after the polymer
151 conditioning/flocculation.

2.4. Adsorption isotherm

Four kinds of adsorption-isotherm models, namely Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm [29], were selected to describe the adsorption equilibrium for both DAS and LAS. The equilibrium time for DAS and LAS was determined from the batch test and the jar test, respectively. For the DAS, the adsorption isotherm experiment was carried out with different glyphosate concentration ranged from 50 to 100 mg/l, particle size <0.063 mm, natural pH (5.2-5.6) of the glyphosate aqueous solution and fixed alum sludge mass of 5 g/l in a series of 100 ml plastic bottles. This test was conducted in duplicate. While for the LAS, the equilibrium data were derived directly from the jar test after the equilibrium was reached.

2.5. Monitoring of glyphosate

Concentration of glyphosate can be indirectly determined through total phosphorus measurement. From the molecule formula of glyphosate, $C_3H_8NO_5P$, a theoretic liner relationship between total phosphorus and glyphosate can be obtained as:

$$y = 5.454x \quad (1)$$

Where y is the concentration of glyphosate (mg/l); x is the concentration of total phosphorus (mg/l, as P). The observed relationship between total phosphorus and glyphosate is in good accordance with the theoretical calculation from the formula (data and plotting not shown), which justified the accuracy of the monitoring method. Measurement of total phosphorus was conducted according to *Standard Methods for the Examination of Water and Wastewater (1998)* [30] using a Helios Alpha UV-Vis Spectrophotometer (Thermo Scientific, England) with 1 cm quartz cells. Samples were filtered through 0.45 μ m diameter Millipore filter paper before the total phosphorus was measured.

3. Results and discussion

3.1. Glyphosate adsorption on DAS and LAS

The glyphosate adsorption on DAS is shown in Fig. 1. The equilibrium was reached after 52 hrs on all the conditions investigated. A highest removal efficiency of 91.6% was obtained

181 at pH 4.3, particle size <0.063 mm and DAS dosage 5 g/l (Fig. 1(a)). The removal efficiency
182 was decreased significantly with the pH increase, it was reduced to 65.4% at pH 9.0, implying
183 that acidic condition is more favorable to the adsorption process. This may suggest the
184 glyphosate adsorption on DAS is more likely a physical process since glyphosate exists in
185 molecular form under acidic condition. Fig. 1(b) shows the effects of particle size on the
186 glyphosate adsorption. The highest removal efficiency of 86.5% was observed at particle size
187 <0.063 mm, and it was dropped to 34.5% at particle size of 1-2 mm due to the decrease of the
188 specific surface area, indicating the adsorption is largely dependent on the particle size.
189 However, the adsorption rate was more or less the same between particle size of 0.425-0.6
190 mm and 1-2 mm. The effect of alum sludge mass on the glyphosate adsorption rate is
191 illustrated in Fig. 1(c). As expected, the larger amount of glyphosate was immobilized with
192 the higher dosage/mass of the alum sludge. But the equilibrium time (as set as 52 hrs) was
193 found to be independent of the alum sludge mass in the range studied since there was no
194 further reduction of glyphosate concentration after 40 hrs adsorption in all cases of the sludge
195 mass adopted.

196 **[Insert Fig. 1 here]**

197
198 Figs. 2(a) and 2(b) show the glyphosate adsorption onto LAS at two different LAS
199 concentrations of 3 g/l and 5 g/l, respectively. The removal efficiency of 64.7-81.8% and
200 89.4-97.4% was obtained for LAS concentration of 3 g/l and 5 g/l, with the adsorbed mass of
201 glyphosate as 81.75-161.85 mg and 97.5-223.50 mg, respectively. The high removal
202 efficiencies obtained under the high initial glyphosate concentrations (200-500 mg/l)
203 indicated that the LAS may have the potential to deal with high strength glyphosate
204 wastewater, such as wastewater produced from glyphosate production process. Furthermore,
205 for almost all the conditions tested, the equilibrium was reached within 1 h, showing the rapid
206 glyphosate adsorption rate onto the LAS.

207 **[Insert Fig. 2 here]**

208
209 The results from Fig.1 and Fig. 2 have demonstrated that both the DAS and LAS can
210 effectively remove glyphosate. In particular, LAS seems to adsorb P more rapidly. This may
211 be due to the fact that LAS has fine particle distribution, which can be visibly observed from
212 Fig. 3. It should be noted that the current study aimed to explore the feasibility of using alum
213 sludge (DAS and LAS) as an easily, locally available material to immobilize the glyphosate,

214 rather than to characterize the alum sludge itself, which has been investigated in our previous
215 studies [23, 24, 26]. Although alum sludge is formed mainly with turbidity (clay, soil), colour,
216 humic substances in the source water being treated, aluminium is a major component and
217 accounted for 8.1% by composition of the sampled alum sludge. Aluminium is known to play
218 a key role in P adsorption/precipitation by solid matrices via ligand exchange [23] and by
219 phosphate ion reactions with aluminium oxides forming inner-sphere complexes [18].

220 **[Insert Fig. 3 here]**
221

222 *3.2. Adsorption equilibrium with different isotherm models*

223 Four equilibrium isotherms were employed to describe the adsorption behaviour. The results
224 of the parameters together with the correlation coefficient (R^2) values of the four isotherms
225 are summarized in Table 1 (experimental data not shown). The Langmuir isotherm fitted the
226 experimental data best for both the DAS and LAS with $R^2 > 0.99$. The value of Q_0 in the
227 Langmuir isotherm, which represents the maximum adsorption capacity, was determined as
228 85.9 mg/g for DAS and 113.6 mg/g for LAS, respectively. This clearly indicates that LAS
229 holds better ability for glyphosate adsorption than DAS, though LAS and DAS contain the
230 same type of solid. The difference in adsorption capacity may be attributed to much smaller
231 particle size and the concomitant large specific surface area of the LAS (10-30 μm) [31],
232 compared with that of DAS used in this study. The Temkin isotherm also fitted the
233 experimental data well for both the DAS and LAS with $R^2 > 0.95$. The Freundlich isotherm
234 seems to fit the DAS data better than LAS data, while the Dubinin-Radushkevich isotherm
235 exhibited an opposite situation, i.e. it fits the LAS data better than that of fitting DAS data.

236 **[Insert Table 1 here]**
237

238 *3.3. Adsorption kinetics*

239 It has been well documented that the adsorption of phosphorus could be well described by
240 the pseudo second-order equation [32]. Considering glyphosate being a kind of phosphorus
241 species in nature, the pseudo second-order equation was chosen to describe the adsorption
242 dynamics in this study. The linear form of the pseudo second-order model is expressed as:

243
$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{kq_e^2} \quad (2)$$

244 Where q_e and q_t are respectively the amount of adsorbate adsorbed at equilibrium and at time t
245 (mg/g); k is the rate constant of pseudo second-order adsorption (g/mg·h). By plotting t/q_t
246 versus t , the second-order rate constant k and constant q_e can be determined.

247 Table 2 lists the kinetics constants of the pseudo second-order model from this study
248 (experimental data not shown). The correlation coefficients were greater than 0.99 for all the
249 different conditions with only exceptions at particle sizes of 0.15-0.212mm and 1-2 mm. This
250 result suggests the good agreement between the experimental data and the pseudo second-
251 order model. All these indicate that glyphosate adsorption kinetics onto the alum sludge can
252 be described by the pseudo second-order model. It should be noted from Table 2 that the
253 kinetics constants varied considerably with the adsorption conditions (pH, particle size, alum
254 sludge mass and alum sludge type etc). Therefore, it is reasonable to suggest that, from the
255 adsorption process design point of view, the relationship between the kinetics parameters and
256 the reaction conditions should be further investigated.

257 **[Insert Table 2 here]**

259 *3.4. Comparison of alum sludge with other adsorbents for glyphosate adsorption*

260 It is noted that glyphosate adsorbed onto other materials has been reported in the literature.
261 Such the materials include different types of soils [33-39], humic substances [40, 41], clay
262 minerals [42-44], layered double hydroxides (LDH) [45, 46] and commercial active carbon
263 [28]. Glyphosate adsorption capacity is usually determined by Langmuir and Freundlich
264 isotherms, but often calculated on different basis in different studies, such as mg/kg, mg/g or
265 mmol/g for q_e . A comparison of glyphosate adsorption capacity on alum sludge with other
266 reported adsorbents based on mg/g for q_e and mg/l for C_e was made in Table 3. It shows that
267 the glyphosate adsorption capacity on alum sludge is much higher than that of the most soils,
268 except for the results reported by Kogan [35] and Yu and Zhou [37]. Humic substances and
269 clay minerals have significant low capacity for glyphosate adsorption compared with the alum
270 sludge. LDH has the comparable capacity to the alum sludge. Active carbon has the same
271 order of magnitude with the alum sludge in glyphosate adsorption capacity, but still lower

272 than the latter. However, in terms of availability and cost, alum sludge is an easily, locally and
273 largely available “waste” by-product in global scale [22]. The LDH and active carbon are
274 least economic and available since they have to be artificially synthesized or produced.
275 Although soils, humic substances and clay mineral are also largely available in nature, alum
276 sludge has the advantage regarding the “waste” reuse and the sustainable development.
277 Overall alum sludge has exhibited the potential to be an efficient and low-cost adsorbent for
278 glyphosate immobilization.

279 [Insert Table 3 here]
280

281 3.5. Effect of sludge conditioning on glyphosate removal

282 Fig. 4 illustrates the turbidity, SS and glyphosate removal under different dosages of
283 polymer LT25 with the stabilized LAS from the Jar tests. The minimum supernatant turbidity
284 of the polymer conditioned LAS was obtained at the polymer dosage of 5 mg/l for both the
285 stabilized LAS with different concentrations. The minimum supernatant turbidity was 60
286 NTU for LAS of 1.2 g/l and 86 NTU for LAS of 2.0 g/l, respectively. The minimum SS of 43
287 mg/l was obtained at the polymer dosage of 1 mg/l for LAS of 1.2 g/l, while the lowest SS of
288 63 mg/l was observed at the polymer dosage of 5 mg/l for LAS of 2 g/l. Interestingly, under
289 the various polymer dosages, the concentration of glyphosate remained more or less the same
290 level around 46 mg/l for LAS of 1.2 g/l and 26 mg/l for LAS of 2 g/l, respectively. It is noted
291 that such the glyphosate concentrations were comparable to the residual glyphosate of 54.4
292 mg/l and 20.8 mg/l in the stabilized LAS samples without polymer addition. Therefore, it
293 seems that the optimal polymer dosage is 5 mg/l regarding the conditioning of the glyphosate-
294 rich LAS. More importantly, it can be concluded that the flocculation/conditioning process
295 could not promote further removal of glyphosate. Fig. 5 illustrates the supernatant of the
296 polymer conditioned LAS (after 1 minute settlement), it gives a visible observation of the
297 effect of polymer dosage on glyphosate-rich LAS conditioning.

298 [Insert Fig. 4 here]

299 [Insert Fig. 5 here]
300

301 4. Conclusions

302 Alum sludge has exhibited the potential to be an efficient and cost-effective adsorbent for

303 glyphosate removal with excellent immobilization ability in this study. The maximum
304 glyphosate adsorption capacity computed by Langmuir isotherm is 85.9 mg/g DAS and 113.6
305 mg/g LAS, respectively, which is comparable to LDH and much higher than humic
306 substances, clay minerals and the most types of soils. From an economic point of view, the
307 concept of “waste” reuse and the feature of alum sludge’s large availability make the alum
308 sludge more advantageous than any other adsorbents. The polymer (LT25) conditioning of the
309 glyphosate-enriched LAS cannot lead to the further reduction of the glyphosate in the
310 supernatant of the dewatered LAS after conditioning. Finally, good agreement between the
311 predicted and the experimental adsorption profiles suggests that the pseudo second-order
312 model can be applied in system and process design.

313

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319

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448 **Tables**

449

450 **Table 1**

451 Isotherm parameters for DAS (particle size of <0.063 mm) and LAS at room temperature
 452 (22 °C) and pH 5.2-5.6

Model isotherm	Linear equation	Parameter	DAS(mean±S.D., n=2)	LAS
Langmuir				
$q_e = \frac{Q_0 b C_e}{1 + b C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{b Q_0}$	Q_0 (mg/g)	85.875±2.609	113.636
		b (1/mg)	0.212±0.040	0.096
		R^2	0.9904	0.9988
Freundlich				
$q_e = K_F C_e^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	K_F (l/g)	5.162±0.649	30.116
		$1/n$	0.285±0.041	0.264
		R^2	0.9552	0.8851
Temkin				
$q_e = \frac{RT}{b_T} \ln(AC_e)$	$q_e = B \ln A + B \ln C_e$	A	3.484±1.365	2.200
		B	2.307±0.769	18.698
		R^2	0.9513	0.9534
Dubinin-Radushkevich				
$q_e = q_m e^{-\beta \varepsilon^2}$	$\ln q_e = \ln q_m - \beta \varepsilon^2$	q_m (mg/g)	14.607±1.024	106.102
		β	0.0016±4.950E-4	0.0024
		R^2	0.8687	0.9872

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465 **Table 2**

466 Kinetics parameters of the second-order model for glyphosate adsorption onto DAS and LAS
 467 under different conditions

Conditions	Kinetics parameters		
	q_e (mg/g)	k	R^2
DAS			
Initial pH			
4.3	9.44	0.0686	0.9998
5.6	9.60	0.0188	0.9933
7.0	8.59	0.0177	0.9910
9.0	7.11	0.0282	0.9916
Particle size (mm)			
<0.063	9.60	0.0188	0.9933
0.150-0.212	4.95	0.0327	0.9848
0.425-0.6	3.93	0.0403	0.9928
1.0-2.0	3.90	0.0358	0.9869
DAS mass (mg/l)			
0.5	34.13	0.0078	0.9977
1	24.81	0.0083	0.9954
3	13.26	0.0129	0.9943
5	9.60	0.0188	0.9933
LAS			
LAS 3 g/l, Initial glyphosate (mg/l)			
200	55.25	1.6745	0.9995
300	79.37	0.0756	0.9982
400	101.01	0.0408	0.9993
500	117.65	0.0190	0.9957
LAS 5 g/l, Initial glyphosate (mg/l)			
200	39.06	0.2341	0.9996
300	58.14	0.1479	0.9998
400	76.92	0.0604	0.9996
500	90.09	0.0342	0.9983

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Table 3

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Comparison of glyphosate adsorption capacity with other adsorbents from the literature

Adsorbent	Langmuir Q_0 (mg/g)	Freundlich K_F (l/g)	Adsorption Conditions	Reference
DAS	85.9	5.2	pH 5.2, particle size <0.063 mm , T 22 °C, equilibrium time 52h, initial glyphosate 50-100 mg/l, solid/solution 0.5g/100ml	This study
LAS	113.6	30.1	pH 5.2, T 22 °C, equilibrium time 24 h, initial glyphosate 200-500 mg/l, solid/solution 2.5g/500ml	This study
Soils	1.6-4.6	—	T 20 °C, equilibrium time 2 h, initial glyphosate 50-300 mg/l, solid/solution 1g/25ml	[33]
Soils	—	0.0006-0.0785	pH4.83-10.4, particle size <2 mm , T 22 °C, equilibrium time 24 h, initial glyphosate 0.03-67 mg/l, solid/solution 0.5g/10ml	[34]
Soils	5.7-231.9	—	pH 4.79-7.76, particle size <1 mm, T 20 °C, equilibrium time 4h, initial glyphosate 1000-2500 mg/l, solid/solution 3g/30ml	[35]
Soils	—	0.04-0.303	pH 5.2-8.1, room temperature, equilibrium time 16h, initial glyphosate 2-10 mg/l, solid/solution 10g/50ml	[36]
Soils	—	42.1-50.3	pH 6.0-6.2, particle size <0.15 mm, T 25 °C, equilibrium time 24h, initial glyphosate 0-250 mg/l, solid/solution 1g/100ml	[37]
Soils	2.6-21.4	—	pH 5.3-5.9, equilibrium time 48h, initial glyphosate 0-2 mmol/l, solid/solution 2g/50ml	[38]
Soils	—	0.021-0.087	pH 6.3-7.5, equilibrium time 70h, initial glyphosate 0.1-10 mg/l, solid/solution 1g/10ml	[39]
Humic	1.1-11.9	0.007-0.454	pH 3, room temperature	[41]
Humic	—	0.003-0.017	pH 2-7, equilibrium time 70h, initial glyphosate 0.2-20 mg/l, solid/solution 10mg/1-2ml	[39]
Clay minerals	—	0.008-0.138	particle size < 0.83mm (20 mesh), room temperature, equilibrium time 1h, solid/solution 0.5-1.0g/25ml	[43]
MgAl-LDH	27.4-184.6	—	pH 5.6-13.1, T 25 °C, equilibrium time 24h	[45]
Ni ₂ AlNO ₃ -	172.4	—	pH 7, T 25 °C, equilibrium time 24h,	[46]

LDH			solid/solution 50mg/50ml	
Active carbon	58.4	—	pH 1.4, particle size 0.21-0.42 mm, T 20 °C, equilibrium time 100min, initial glyphosate 2-15 mg/l, solid/solution 10g/100ml	[28]

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Figure caption:

Fig. 1. Glyphosate adsorption onto DAS under, (a) different initial pH (at DAS of 5 g/l and particle size of <0.063 mm), (b) different particle size (at DAS of 5 g/l and pH 5.6), and (C) different alum sludge mass (at particle size of <0.063 mm and pH 5.6)

Fig. 2. Glyphosate adsorption onto LAS under different initial glyphosate concentrations with LAS of 3 g/l (a), and LAS of 5 g/l (b) at room temperature (22 °C) and the natural pH (5.2) of the glyphosate aqueous solution

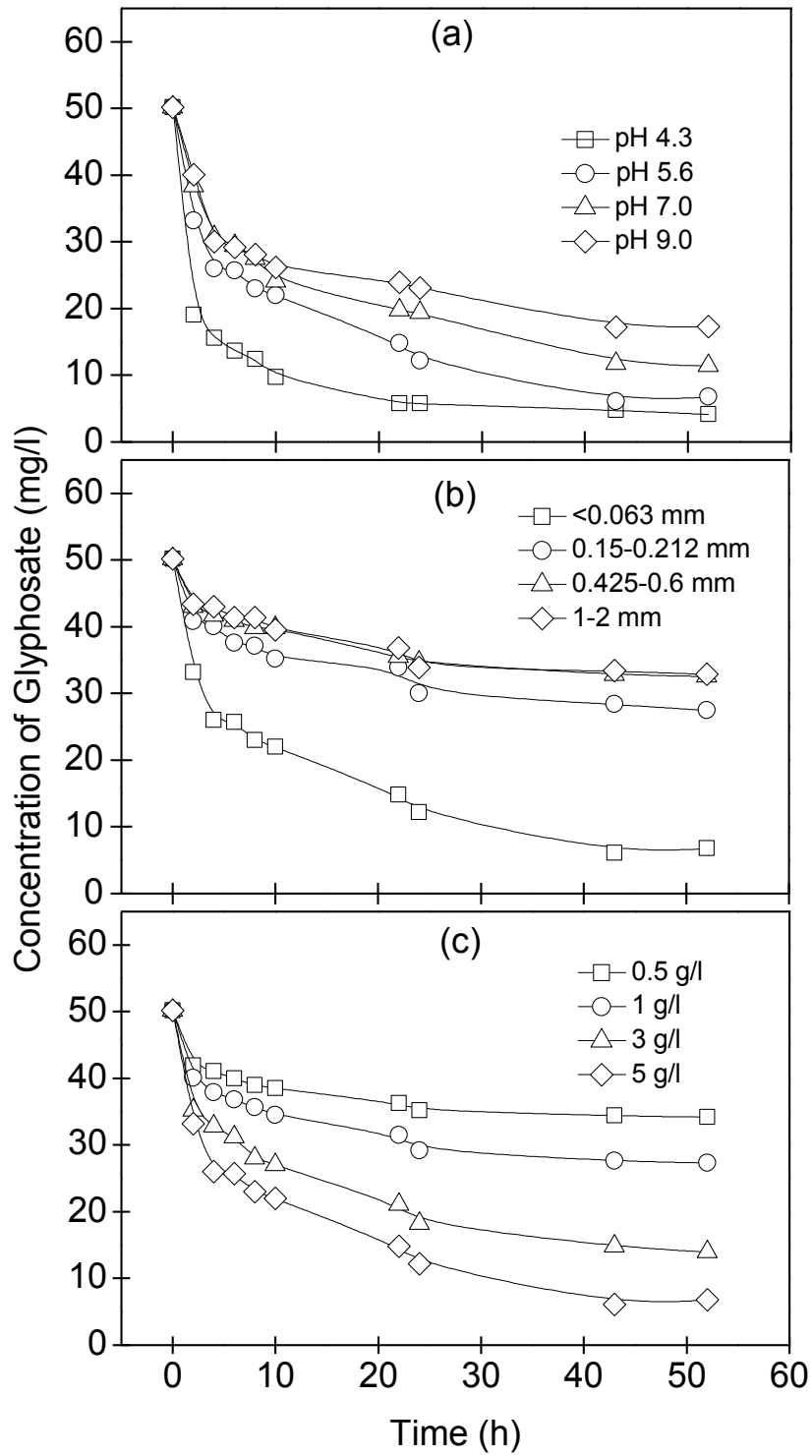
Fig. 3. Close shot of the DAS and the LAS used in this study

Fig. 4. Polymer conditioning of glyphosate-rich LAS at concentration of 1.2g /l (a), and 3 g/l (b)

Fig. 5. Supernatant of the glyphosate-rich LAS after 1 minute settlement of the polymer conditioning at LAS concentration of 1.2g /l (a), and LAS of 2 g/l (b) (Label on each of the tube indicates the polymer dosage.)

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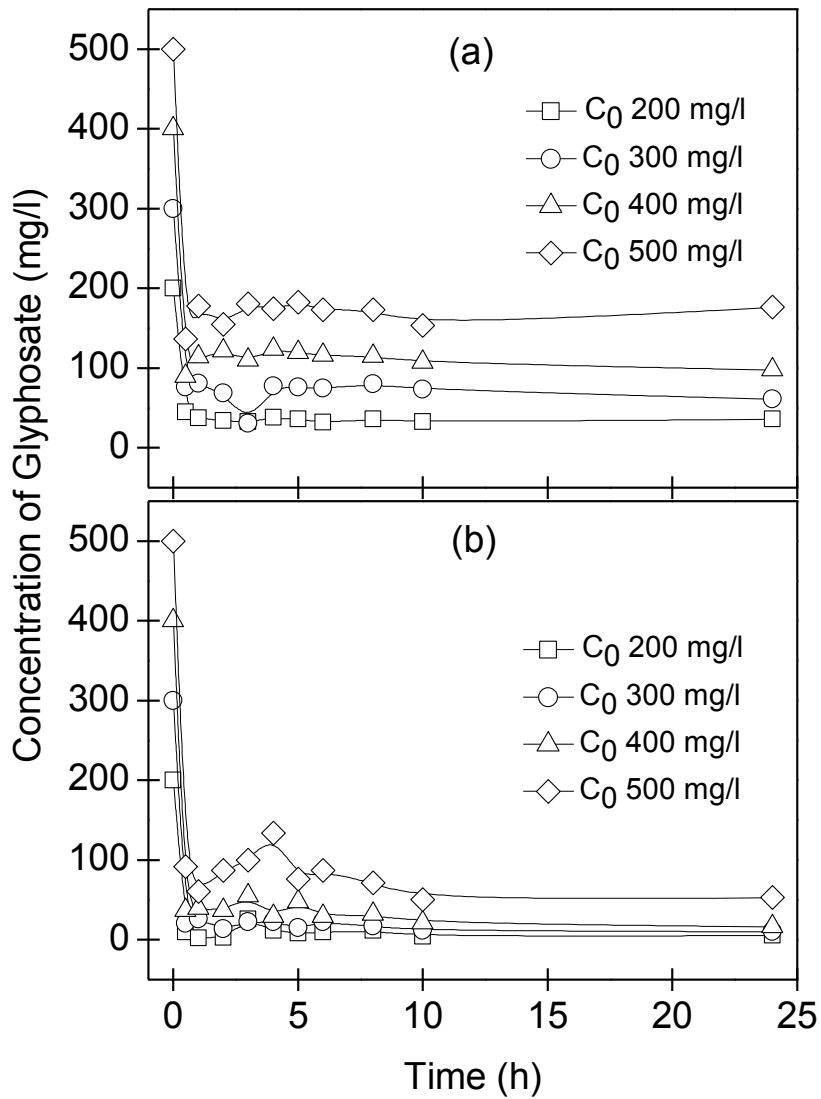
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Fig. 1.

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Fig. 2.

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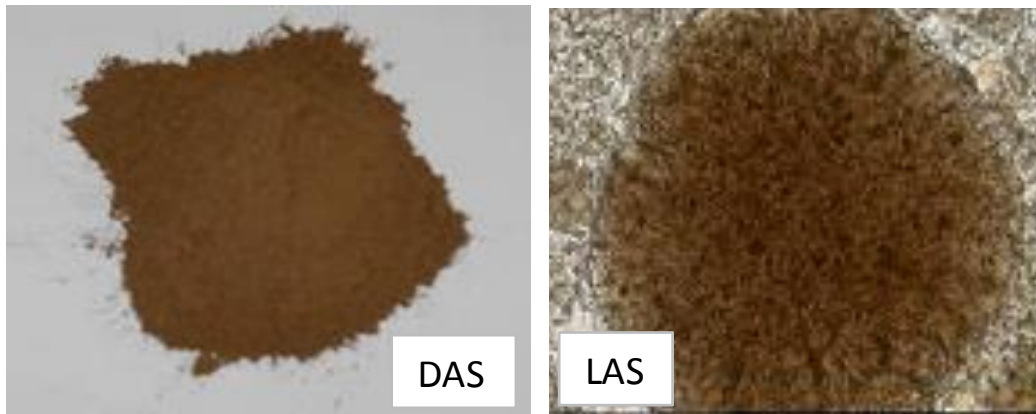
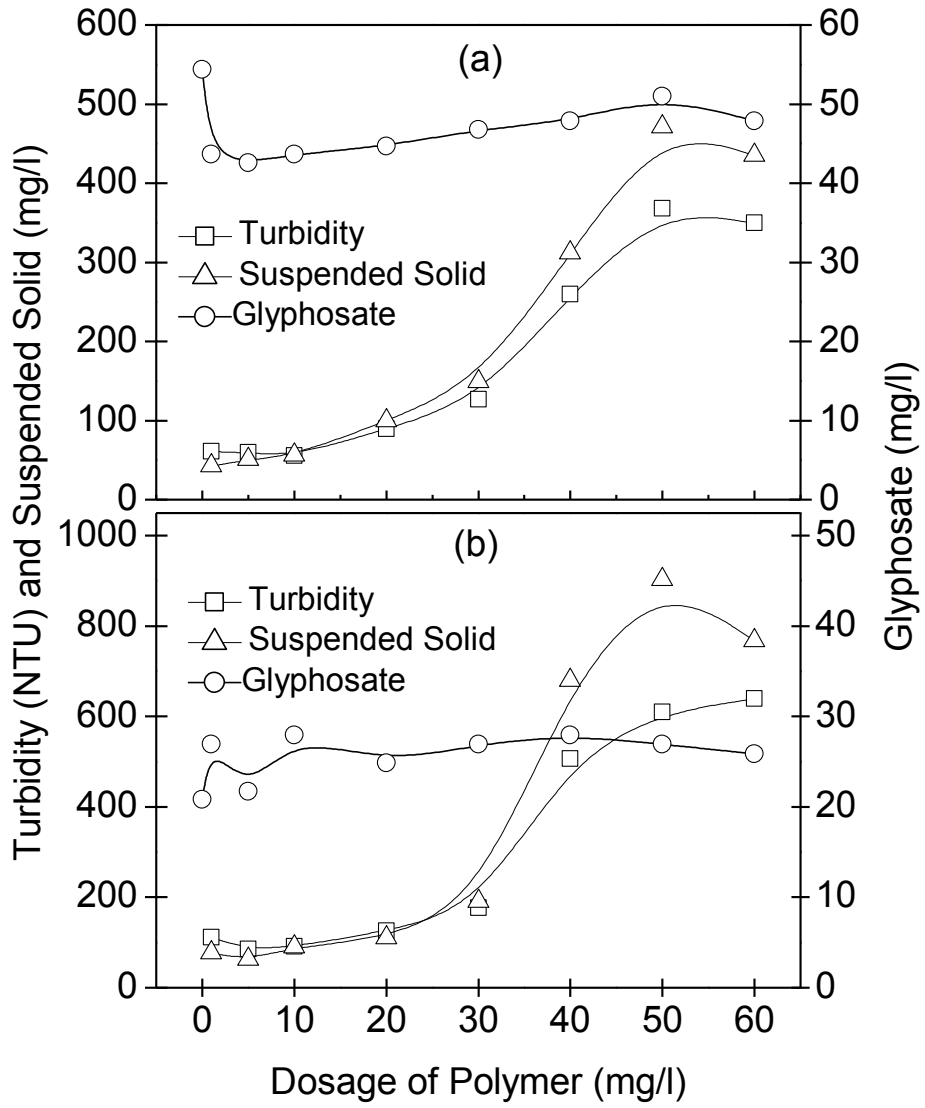


Fig. 3.

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Fig. 4.

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Fig. 5.