Research Repository UCD

Title	Removal of glyphosate from aqueous environment by adsorption using water industrial residual
Authors(s)	Hu, Y.S., Zhao, Y.Q., Sorohan, B.
Publication date	2011-04
Publication information	Hu, Y.S., Y.Q. Zhao, and B. Sorohan. "Removal of Glyphosate from Aqueous Environment by Adsorption Using Water Industrial Residual" 271, no. 1–3 (April, 2011).
Publisher	Elsevier
Item record/more information	http://hdl.handle.net/10197/3113
Publisher's statement	This is the author's version of a work that was accepted for publication in Desalination. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Desalination, 271 (1-3): 150-156 DOI: 10.1016/j.desal.2010.12.014.
Publisher's version (DOI)	10.1016/j.desal.2010.12.014

Downloaded 2023-04-07T10:52:29Z

The UCD community has made this article openly available. Please share how this access benefits you. Your story matters! (@ucd_oa)

© Some rights reserved. For more information

Removal of glyphosate from aqueous environment by adsorption using water industrial residual

Y. S. Hu^a, Y. Q. Zhao^{a,*}, B. Sorohan^b

^a Centre for Water Resources Research, School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland

^b School of Biology & Environmental Science, University College Dublin, Belfield, Dublin 4, Ireland

*Corresponding author; Tel: +353-1-7163215; Fax: +353-1-7167399

E-mail: yaqian.zhao@ucd.ie

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

Keywords: adsorption, adsorption isotherm, alum sludge, glyphosate, reuse, water treatment residual

1. Introduction

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

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

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

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

Thus, the aim of this study is to justify the feasibility of the alum sludge for glyphosate immobilization. This will, of course, promote the beneficial reuse of alum sludge in wide range of pollutant control in environmental engineering. Alum sludge in the forms of dewatered alum sludge (DAS) cake and liquid alum sludge (LAS) has been used for glyphosate adsorption tests. Firstly, batch tests were carried out to investigate the factors that affect the glyphosate adsorption onto alum sludge and provide information, such as equilibrium time and suitable initial glyphosate concentration range for the ensuing equilibrium studies. Secondly, the adsorption equilibrium studies with different adsorption isotherm models were conducted to determine the maximum adsorption capacity. Adsorption kinetics of the glyphosate onto alum sludge was also studied. In addition, polymer conditioning of glyphosate saturated LAS (after adsorption tests) was implemented with Magnafloc LT25 for the purposes of sufficient solid-liquid separation and exploring any 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 $C_3H_8NO_5P$ 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

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

2.3. Jar test with LAS

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

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

[Insert Fig. 1 here]

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

[Insert Fig. 2 here]

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

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

[Insert Fig. 3 here]

3.2. Adsorption equilibrium with different isotherm models

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

[Insert Table 1 here]

3.3. Adsorption kinetics

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

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

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

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

[Insert Table 2 here]

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

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

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

[Insert Table 3 here]

3.5. Effect of sludge conditioning on glyphosate removal

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

[Insert Fig. 4 here]

[Insert Fig. 5 here]

4. Conclusions

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

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

Acknowledgements

The authors would like to thank Irish Environmental Protection Agency for financial support for this study through projects grants (no: 2005-ET-S-7-M3 and 2005-ET-MS-38-M3). Ballymore-Eustace Water Treatment Plant is also thanked for kind assistance of providing alum sludge.

References

- [1] A.T. Woodburn Glyphosate: production, pricing and use worldwide. *Pest Manag. Sci.* 56 (2000) 309-312.
- [2] D. Buffin and J. Topsy. Health and environmental impacts of glyphosate: The implications of increased use of glyphosate in association with genetically modified crops. *Friends of the Earth*, London, 2001.
- [3] C. Cox. Glyphosate. *J. Pestic. Reform* 11(2) (1991)35-38.
- [4] K. Solomon and D. Thompson. Ecological risk assessment for aquatic organisms from over-water uses of glyphosate. *J. Toxicol. Environ. Health B* 6(3) (2003) 289-324(36).
- [5] R.A. Relyea. The lethal impact of roundup on aquatic and terrestrial amphibians. *Ecol. Appl.* 15(4) (2005) 1118-1124.
- [6] N. Benachour and G.-E. S éralini. Glyphosate formulations induce apoptosis and necrosis in human umbilical, embryonic, and placental cells. *Chem. Res. Toxicol.* 22(1) (2009) 97–105.
- [7] M.-W. Ho and B. Cherry. Death by multiple poisoning, glyphosate and roundup.

<http://www.i-sis.org.uk/DMPGR.php> (accessed 11 Feb 2009).

- [8] Directive 98/83/EC of the European Parliament and of the Council of 3 November 1998 on the quality of water intended for human consumption. Official Journal L 330, 05/12/1998.
- [9] M.T. Wan, J.N. Kuo, B. McPherson and J. Pasternak. Agricultural pesticide residues in farm ditches of the Lower Fraser Valley, British Columbia, Canada. *J. Environ. Sci. Health B* 41(5) (2006) 647-669.
- [10] J. Struger, D. Thompson, B. Staznik, P. Martin, T. McDaniel and C. Marvin. Occurrence of glyphosate in surface waters of Southern Ontario. *Bull. Environ. Contam. Toxicol.* 80(4) (2008) 378-384.
- [11] W.A. Battaglin, K.C. Rice, M.J. Focazio, S. Salmons and R.X. Barry . The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005–2006. *Environ. Monit. Assess.* 155 (2009) 281–307.
- [12] A.B. William, C.R. Karen, J.F. Michael, S. Sue and X.B. Robert. The occurrence of glyphosate, atrazine, and other pesticides in vernal pools and adjacent streams in Washington, DC, Maryland, Iowa, and Wyoming, 2005–2006. *Environ Monit. Assess* 155 (2009) 281–307.
- [13] Y. Mason, E. Choshen and C. Rav-Acha. Carbamates insecticides: Removal from water by chlorination and ozonation. *Water Res.* 24 (1990) 11-21.
- [14] T.F. Speth. Glyphosate removal from drinking water. *J. Environ. Eng.* 119(6) (1993) 1139-1157.
- [15] S. Chen and Y. Liu . Study on the photocatalytic degradation of glyphosate by TiO₂ photocatalyst. *Chemosphere* 67 (2007) 1010-1017.
- [16] J.G. Kim, J.H. Kim, H.S. Moon, C.M. Chon and J.S. Ahn. Removal capacity of water plant alum sludge for phosphorus in aqueous solutions. *Chem. Speciat. Bioavailab.* 14 (2002) 67–73.
- [17] E.A. Dayton, N.T. Basta, C.A. Jakober and J.A. Hattey. Using treatment residuals to reduce phosphorus in agricultural runoff. *J. Am. Water Works Assoc.* 95(4) (2003) 151–158.
- [18] J.A. Ippolito, K.A. Barbarick, D.M. Heil, J.P. Chandler and E.F. Redente. Phosphorus retention mechanisms of a water treatment residual. *J. Environ. Qual.* 32(5) (2003) 1857–1864.
- [19] D.A. Georgantas and H.P. Grigoropoulou. Phosphorus removal from synthetic and municipal wastewater using spent alum sludge. *Wat. Sci. Tech.* 52(10–11) (2005) 525–532.
- [20] K.C. Makris, W.G. Harris, G.A. O'Connor, T.A. Obreza and H.A. Elliott. Physicochemical properties related to long-term phosphorus retention by drinking-water treatment residuals. *Environ. Sci. Technol.* 39(11) (2005) 4280-9.
- [21] M.M. Mortula and G.A. Gagnon. Alum residuals as a low technology for phosphorus removal from aquaculture processing water. *Aquacult. Eng.* 36 (2007) 233–238.

- [22] A.O. Babatunde and Y.Q. Zhao. New low-cost wastewater treatment system pioneered in Ireland. *Proceedings of the Institution of Civil Engineers-CIVIL ENGINEERING* 162(4) (2009) 148.
- [23] Y. Yang, Y.Q. Zhao, A.Q. Babatunde, L. Wang, Y.X. Ren and Y. Han. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Sep. Purif. Technol.* 51(2) (2006) 193-200.
- [24] Y. Yang, Y.Q. Zhao and P. Kearney. Influence of ageing on the structure and phosphate adsorption capacity of dewatered alum sludge. *Chem. Eng. J.* 145(2) (2008) 276-284.
- [25] M. Razali, Y.Q. Zhao and M. Bruen. Effectiveness of a drinking-water treatment sludge in removing different phosphorus species from aqueous solution. *Sep. Purif. Technol.* 55(3) (2007) 300-306.
- [26] A.O. Babatunde, Y.Q. Zhao, A.M. Burke, M.A. Morris and J.P. Hanrahan. Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands. *Environ. Pollut.* 157(10) (2009) 2830-2836.
- [27] Y.Q. Zhao, A.O. Babatunde, X.H. Zhao and W.C. Li. Development of alum sludge-based constructed wetland: An innovative and cost-effective system for wastewater treatment. *J. Environ. Sci. Health A* 44(8) (2009) 827-832.
- [28] L.-J. Shen, Q.-H. Le, Y.-Z. Yang and Y.-H. Shi. Static absorption of glyphosate by active carbon. *Chem. Eng.* 10 (2006) 46-49 (in Chinese).
- [29] Y.Q. Zhao, M. Razali, A.O. Babatunde, Y. Yang and M. Bruen. Reuse of Aluminium-based water treatment sludge to immobilize a wide range of phosphorus contamination: Equilibrium study with different isotherm models, *Sep. Sci. Technol.* 42(12) (2007) 2705-2721.
- [30] APHA, *Standard Methods for the Examination of Water and Wastewater*, 20th ed, American Public Health Association, Washington DC, USA, 1998
- [31] Y.Q. Zhao and D.H. Bache. Polymer impact on filter blinding during alum sludge filtration. *Water Res.* 36 (2002) 3691-3698.
- [32] M. Özacar. Equilibrium and kinetic modelling of adsorption of phosphorus on calcined alunite. *Adsorption* 9(2) (2003) 125-132.
- [33] A. Piccolo, G. Celano, M. Arienzo and A. Mirabella. Adsorption and desorption of glyphosate in some European soils. *J. Environ. Sci. Health B* 29 (1994) 1105-1115.
- [34] H. De Jonge and L.W. De Jonge. The influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. *Chemosphere* 39(5) (1999) 753-763.
- [35] M. Kogan, A. Metz and R. Ortega. Adsorption of glyphosate in Chilean soils and its relationship with unoccupied phosphate binding sites. *Pesq. Agropec. Bras.* 38(4) (2003) 513-519.
- [36] S. Autio, K. Siimes, P. Laitinen, S. Ramo, S. Oinonen and L. Eronen. Adsorption of sugar beet herbicides to Finnish soils. *Chemosphere* 55 (2004) 215-226.

- [37] Y. Yu and Q.-X. Zhou. Adsorption characteristics of pesticides methamidophos and glyphosate by two soils. *Chemosphere* 58 (2005) 811–816.
- [38] A.L. Gimsing, C. Szilas and O.K. Borggaard. Sorption of glyphosate and phosphate by variable-charge tropical soils from Tanzania. *Geoderma* 138 (2007) 127–132.
- [39] C.N. Albers, G.T. Banta, P.E. Hansen and O.S. Jacobsen. The influence of organic matter on sorption and fate of glyphosate in soil-Comparing different soils and humic substances. *Environ. Pollut.* 157 (2009) 2865-2870.
- [40] Y.A. Madhun, V.H. Freed and J.L. Young. Binding of ionic and neutral herbicides by soil humic acids. *Soil Sci. Soc. Am. J.* 50 (1986) 319–322.
- [41] A. Piccolo, G. Celano and P. Conte. Adsorption of glyphosate by humic substances. *J. Agric. Food Chem.* 44(8) (1996) 2442-2446.
- [42] P. Sprankle, W.F. Meggitt and D. Penner. Adsorption, mobility and microbial degradation of glyphosate in the soil. *Weed Sci.* 23 (1975) 229–234.
- [43] R.L. Glass . Adsorption of glyphosate by soils and clay minerals. *J. Agric. Food Chem.* 35(4) (1987) 497-500.
- [44] H.M. Dion, J.B. Harsh and H.H. Hill. Competitive sorption between glyphosate and inorganic phosphate on clay minerals and low organic matter soils. *J. Radioanal. Nucl. Chem.* 249(2) (2001) 385–390.
- [45] F. Li, Y. Wang, Q. Yang, D.G. Evans, C. Forano and X. Duan. Study on adsorption of glyphosate (N-phosphonomethyl glycine) pesticide on MgAl-layered double hydroxides in aqueous solution. *J. of Hazard. Mater.* 125(1-3) (2005) 89-95.
- [46] A. Khenifi, Z. Derriche, C. Mousty, V. Pr'evot and C. Forano . Adsorption of glyphosate and glufosinate by Ni₂AlNO₃ layered double hydroxide. *Appl. Clay Sci.* 47(3-4) (2010) 362-371.

Tables

Table 1

Isotherm parameters for DAS (particle size of <0.063 mm) and LAS at room temperature (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

Table 2

Kinetics parameters of the second-order model for glyphosate adsorption onto DAS and LAS 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

479

Table 3

480

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	pH 4.83-10.4, 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]

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.)

503

504

Fig. 1.

505

506

507

508
509

Fig. 2.

510
511
512
513
514
515
516
517
518

519
520
521

522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541

Fig. 3.

Fig. 4.

553
554
555

556
557
558
559
560
561
562
563

Fig. 5.