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# Amine-functionalized, multi-arm star polymers: A novel platform for removing glyphosate from aqueous media

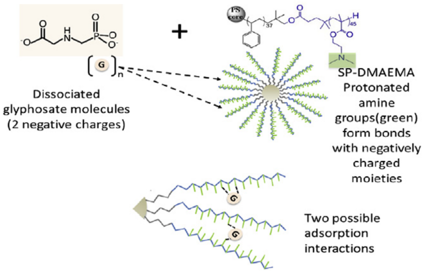
Lianna Samuel*, Ran Wang, Geraud Dubois, Robert Allen, Rudy Wojtecki, Young-Hye La**

*IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120, USA*

## HIGHLIGHTS

- Bioaccumulation of glyphosate ingested in even trace amounts can negatively impact health.
- Rapid, efficient glyphosate adsorption by mesoporous-like star-polymers with high amine functional group aerial density.
- Ionic interactions which promote adsorption are affected by pH.
- Glyphosate removal efficiency is greater than 85% for neutral and slightly basic conditions.
- Maximum glyphosate adsorption capacity is 229.017 mg glyphosate/g star-polymer.

## GRAPHICAL ABSTRACT



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## ABSTRACT:

We describe a novel method for efficiently removing glyphosate from aqueous media via adsorption onto highly functionalized star-shaped polymeric particles. These particles have a polystyrene core with more than 35 attached methacrylate polymer arms, each containing a plurality of pendant amines (poly(-dimethylamino ethyl methacrylate): PDMAEMA) that are partially protonated in water. Kinetic studies demonstrate that these star-polymers successfully remove up to 93% of glyphosate present in aqueous solution (feed concentration: 5 ppm), within 10 min contact time, outperforming activated carbon, which removed 33% after 20 min. On these star-polymers, glyphosate adsorption closely follows the Langmuir model indicating monolayer coverage at most. Ionic interaction between the protonated amines and glyphosate's dissociated carboxylic and phosphoric acid groups lead to effective glyphosate capture even at feed concentrations below 1 ppm. Surface charge of these star polymers and dissociation of glyphosate are both influenced by pH, thus glyphosate removal efficiency increases from 63% to 93% when pH increases from 4.2 to 7.7. NMR studies conducted with butylamine as a proxy for these polymeric particles confirm that the amine group binds with both glyphosate's carboxylic and phosphoric acid groups when its concentrations are in a 2:1 or higher molar ratio with glyphosate.

## 1. Introduction

Population growth has driven the increased use of pesticides and herbicides in agriculture globally, to ensure adequate food supply. Glyphosate [N–(phosphonomethyl) glycine] is the active

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* Corresponding author.
** Corresponding author.
*E-mail addresses:* samuell@us.ibm.com (L. Samuel), yna@us.ibm.com (Y.-H. La).

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ingredient of a broad spectrum, nonselective, post-emergence herbicide. This herbicide is one of the most widely used in the world, controlling the growth of various weeds and grasses (Guo et al., 2005), which can stifle the development of desirable crops, reducing both the quantity and quality of harvests. Glyphosate usage has been largely enhanced by the use of genetically modified crops that are glyphosate-resistant and promote its direct application to these crops as well as targeted weeds and grasses. This widespread use of glyphosate has led to its presence and one of its major metabolite aminomethylphosphonic acid (AMPA) in the environment due to run-off (both during and after its application due to leaching).

Additionally, any applied glyphosate that remains on the harvested crops can be transferred to consumer products by contamination of processing machinery used during their preparation. Thus, traces of glyphosate and AMPA can be found not only in natural waterways but also on fruits and produce available for human consumption (Solomon and Thompson, 2003; Relyea, 2005; Buffin and Jewell, 2014). The presence of glyphosate (in various herbicide formulations) and its metabolite in both our food and drinking water supplies has raised many concerns (Freuze et al., 2007; Ho and Cherry, 2009; Qian et al., 2009; Paganelli et al., 2010). As an herbicide, glyphosate disrupts the shikimate pathway from amino acid biosynthesis in plants (Schönbrunn et al., 2001). However, it has also been found to negatively affect enzyme activity (Freuze et al., 2007), cause cytotoxicity and DNA damage in human cells (Gasnier et al., 2009; Paganelli et al., 2010) and damage to the mammalian endocrine system with prolonged exposure (Richard et al., 2005).

Globally, the allowable concentration of glyphosate in drinking water ranges from 0.1 $\mu gL^{-1}$ (European Union Drinking Water Regulations, for all pesticides) (European Commission, 1991) to 0.7 $mgL^{-1}$ (Environmental Protection Agency drinking water regulatory guidelines) (EPA webpage, accessed 2015). More recently, the World Health Organization announced that glyphosate is a likely carcinogen to humans, as well (Fritschi et al., 2014). Additionally, prolonged exposure to and ingestion of glyphosate even in trace amounts (10 μg/L) has been shown to have devastating effects on kidney health when combined environmental factors such as water hardness and nephrotoxic metals (Jayasumana et al., 2014). Therefore, there is a need to minimize the amount of glyphosate present in drinking water and other food products. However, glyphosate has small molecular weight, high polarity and solubility in water although it is insoluble in organic solvents (Stalikas and Konidari, 2001), making its removal from aqueous solution difficult. Currently, numerous techniques (chlorination, ozonation, photolysis and heterogeneous photocatalysis) are used to reduce glyphosate concentrations in drinking water, either individually or in different combinations (Speth, 1993; Assalin et al., 2009). Obtaining an efficient, affordable method for glyphosate removal is still needed (Hu et al., 2011). Adsorption can be an affordable removal method but most activated carbon, although used in generic water treatment because of their high micro-porosity and degree of surface reactivity are less effective on acidic, hydrophilic and highly soluble compounds like glyphosate (Hamerlinck et al., 1994; Mohan and Pittman, 2006; Bozkaya-Schrotter et al., 2008).

Star–shaped polymers provide a potential solution, they are structurally designed to exhibit high adsorption capacity, with a large number of arms that can be functionalized and fine-tuned to capture specific molecules and form highly microporous structures (Mishra and Kobayashi, 1999). In this work, batch adsorption equilibrium study has been conducted to examine the potential use of in-house prepared, tailored star-polymer particles with high aerial density of amine functional groups and mesoporous-like structure for successfully removing low concentrations of glyphosate from aqueous media. To better understand the relationship of material structure and glyphosate removal efficacy, comparative adsorption studies were also performed with polyamidoamine (PAMAM) dendrimer with numerous amine-functional groups in its terminal positions along with activated carbon (control). Additionally, the adsorption mechanism was also investigated together with the influence of pH, and feed concentration on the overall glyphosate removal efficiency of the star polymer.

## 2. Experimental (materials and methods)

Batch glyphosate adsorption tests were carried out with the amine-functionalized star polymer (SP-PDMAEMA), PAMAM dendrimers (PAMAM6) with ethylenediamine core (generation 6.0, Sigma-Aldrich, WI, USA), and activated carbon (−100 mesh, powder) (Sigma-Aldrich, WI, USA) to investigate the importance of adsorbent structure, chemistry and amine-functional density on glyphosate adsorption. SP-PDMAEMA consists of a hydrophobic core made up of cross-linked polystyrene and hydrophilic methylacrylate polymer arms with a plurality of tertiary amines (ex. Poly (N, *N*-dimethylaminoethyl methacrylate): PDMAEMA) (Fig. 1(a)). The polymer was synthesized via the procedure described in an earlier literature (Lee et al., 2011).

A 10 ppm stock solution of glyphosate was made by dissolving 0.01 g of analytical grade glyphosate powder (Sigma-Aldrich, Pestanal®) in 1 L deionized water (made in house, via reverse osmosis with resistivity of 18.4 million ohm-cm and TDS: ~7 ppm). 250 ml of the glyphosate stock solution was added to 250 ml of deionized water to create a desired initial concentration of 5 ppm. 10 ml aliquots of the 5 ppm glyphosate solution were then placed into a series of 25 ml vials containing 0.005 g of activated carbon, 0.125 ml PAMAM6 dendrimers (5% weight dendrimers in methanol) and 5 ml SP-PDMAEMA solution (0.1% weight SP-PDMAEMA by volume), respectively, to ensure that the same mass of adsorbent was used for each trial. Each trial was repeated four times and the glyphosate concentrations measured were averaged. For each trial, blank deionized water specimens were collected. The adsorption of glyphosate onto SP-PDMAEMA, PAMAM6 and activated carbon was then determined as a function of time and adsorption kinetics determined.

Duplicate studies to determine the effect of pH and initial glyphosate concentration were also conducted using SP-PDMAEMA, to better understand its efficiency. PAMAM6 was not used in the pH study due to its poor performance in capturing glyphosate. To determine the effect of pH on glyphosate adsorption, the initial pH of 5 ppm glyphosate solution was maintained (pH: 7.7, control) and adjusted to 4.2, 8.1 and 11.6 respectively, by adding 0.1 mol/L hydrochloric acid or 0.1 mol/L sodium hydroxide to the glyphosate solution after the addition of SP-PDMAEMA. To determine the effect of varying initial glyphosate concentrations, the stock solution was diluted with deionized water to obtain solutions with glyphosate concentrations ranging from 10 ppm to500 ppb (10, 7.5, 5, 2.5 and 1 ppm and 500 ppb). Two adsorption-isotherm models were selected to aid in describing the adsorption equilibrium for the adsorbents (Langmuir and Freundlich isotherms).

After the glyphosate adsorption, the complexes of glyphosate and SP-PDMAEMA and glyphosate and PAMAM6 were filtered using PS20 filters (polysulfone membrane with 20 kDa molecular weight cut-off, Sepro Membranes Inc.) under a pressure of 25 psi while the complexes of glyphosate and activated carbon were filtered using Acrodisc® 25 mm syringe filters with 1 μm PTFE membranes (Pall Laboratories) attached to 12 ml plastic syringes. These filters were used as tests on the filtrates obtained from pure deionized water passing through these filters did not show any