

Controlled Pesticide Release from Porous Composite Hydrogels Based on Lignin and Polyacrylic Acid

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For the controlled release of pesticides, a novel composite porous hydrogel (LBPAA) was prepared based on lignin and polyacrylic acid for use as the support frame of a pore structure for water delivery. The LBPAA was analyzed to determine its water-swelling and slow release properties. The controlled release properties of LBPAA were evaluated through experiments in relation to the cumulative release of pesticides, with particular emphasis on environmental effects and release models. The porous LBPAA hydrogel showed improved properties compared to polyacrylic acid, and could therefore be considered an efficient material for application in controlled release systems in agriculture.

Keywords: Pesticide; Controlled release; Biodegradable materials; Lignin

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INTRODUCTION

To solve global food shortage issues, the extensive use of pesticides has been required to maximize food production. However, over the decades, this has resulted in severe environmental pollution and ecological issues, as a large amount of applied pesticides often fails to reach their intended targets because of degradation, volatilization, and leaching (Gómez-Martínez *et al.* 2009; Chen *et al.* 2014; Garrido *et al.* 2014). In addition, with the development of economy, society has become more concerned about food security. Consequently, to overcome these problems, controlled release formulations (CRFs) have been considered as a possible alternative to compensate for the loss of effectiveness of conventional pesticide formulations (Bhattarai *et al.* 2010; Chacara *et al.* 2011).

A number of important developments have contributed to the advancement of formulations for the controlled release of chemicals in agriculture (Bruna *et al.* 2009; Dong *et al.* 2011; Mandal *et al.* 2013; Martinez *et al.* 2013). Microencapsulation, for example, has been widely adopted commercially because of its use in concentrated formulations for spraying (Rodham 2000; Pascual-Villalobos *et al.* 2013; Gómez-Martínez *et al.* 2013). In addition, research into natural and biodegradable polymers for use in larger particle-size formulations or devices such as gels, cross-linked polymers, and composites is also of importance (Calabria *et al.* 2012; Mariana and Marta 2014).

Lignin is a low-cost waste product obtained from the paper pulp manufacturing process; it is cheap and readily available. A large amount of lignin is extracted in the production of ethanol and pulp industries. For the purpose of environmental protection and a favorable use of waste, lignin applications are being developed. Lignin can be used as a compatibilizer, plasticizer, or stabilizer (Banu *et al.* 2006; Henry *et al.* 2012; Narapakdeesakul *et al.* 2013). Lignin can also be used to form composites with other materials, thereby modifying their properties. Some lignin is used as a raw material for

isocyanate, epoxy resin, and hydrogel products (Feng *et al.* 2011). In addition, lignin is also a currently underutilized resource that shows great potential for the preparation of controlled release formulations (Mulder *et al.* 2011). Diuron (DCMU, 3-(3,4-dichlorophenyl)-1,1-dimethylurea) is a widely applied herbicide for general weed control in soil, and it has been reported that the adoption of lignin formulations of Diuron could reduce water contamination in soil (Cottefill *et al.* 1996).

The authors previously reported the preparation of porous hydrogels (LBPAA) based on lignin and acrylic acid for application in the controlled release of pesticides. The present study aims at exploring the potential use of lignin with a hydrophobic backbone for modulating transfer properties of LBPAA and designing a new CRF for pesticides. For this purpose, 1,1'-dimethyl-4,4'-bipyridinium dichloride (Paraquat), β -cyfluthrin (cyfluthrin), and cyhalofop-butyl were selected as model pesticides, with the aim of introducing them into a series of LBPAA materials with varying lignin contents *via* an adsorption process. Paraquat, cyfluthrin, and cyhalofop-butyl all contain very different, yet relatively common, organic pesticide structures. Indeed, the adsorption/desorption mechanisms of the pesticides on LBPAA are mostly governed by their polarity and chemical structure. Release experiments were also performed in water, to study the influence of the formulation on both pesticide diffusivity within the material and the partition coefficient between the material and the water. Release properties were also considered in relation to the structure of materials and the effects of environmental factors.

EXPERIMENTAL

Materials

Commercial lignin was supplied by Tralin Paper Co., Ltd. (Shandong, China). Lignin was isolated by alkali-assisted extraction from wheat straw, to give a composition containing 82.69% lignin, 8.35% carbohydrates, and 8.96% ash. The total hydroxyl content of lignin was found to be 2.95 mmol g⁻¹. All reagents were of analytical grade and were used without further purification. Acrylic acid (AA), ammonium persulfate (APS), and *N,N'*-methylenebisacrylamide (MBAm) were obtained from the Aladdin Chemistry Co., Ltd. (Guangzhou, China). Paraquat, cyfluthrin, and cyhalofop-butyl were purchased from the Aladdin Chemistry Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), ferrous sulfate (FeSO₄), anhydrous ethanol (EtOH), and hydrogen peroxide (H₂O₂, 30%) were purchased from Shanghai Reagent Corp. (Shanghai, China). Deionized water with a pH value of approximately 6.9 was used throughout the study.

Methods

Preparation of LBPAA

LBPAA was prepared according to previous research (Ma *et al.* 2012). A lignin solution, 1 g lignin powder dissolved in a solution of NaOH, was heated to 60 °C. FeSO₄ (0.05 g) and H₂O₂ (1 mL) were then added, and the mixture was held at 60 °C for 0.5 h. When the reaction mixture was cooled to 40 °C, a mixture of AA (monomer, 1.56 mL neutralization degree 60%), MBAm (cross-linker, 0.7 wt.%), and APS (initiator, 1 wt.%) were added to the flask. The temperature was then increased to 60 °C and maintained for 2 h under N₂ to complete the polymerization process. The resulting product was washed with anhydrous ethanol and extracted with acetone at 20 °C for 24 h to dissolve the homopolymer and lignin (Ma *et al.* 2012). The hydrogels were then dried to constant weight at 70 °C. Dry LBPAA was ground in a circular cylinder (5 mm diameter, 2 mm

thickness) using a gel puncher (Tiancheng, Shanghai, China). This method was used to prepare materials with polymers and lignin in various mass ratios. Polyacrylic acid (PAA), as a control sample, was also prepared according to the above procedure without the addition of lignin.

Characterization

The morphology of LBPAA was studied using scanning electron microscopy (SEM) (FEI Quanta 200, FEI Ltd., USA). The freeze-dried samples were gold-coated using an accelerating voltage of 10 kV before scanning. The apparent specific surface area was obtained using the Brunauer–Emmett–Teller method (BET). Nitrogen adsorption measured in the relative pressure range from 10^{-6} to 1.0 using ASAP 2020 (77K, Micromeritics Co., USA).

Fourier transform infrared (FTIR) studies were performed using an FTIR-650 spectrometer (Guangdong Ltd., Tianjin, China). The samples were prepared for FTIR analysis by the preparation of KBr pellets (1 mg/100 mg). Resolution of the collected spectra was 16 cm^{-1} .

Pesticide loading content

The LBPAA was compared with PAA to investigate pesticide release. Preparation of pesticide-loaded LBPAA was carried out using paraquat, cyfluthrin, and cyhalofop-butyl as model pesticides. Dry LBPAA (0.1 g) was equilibrated in the desired pesticide solution (100 mL, 0.04%) for 24 h using a shaking water bath incubator. The concentration of the remaining liquid was evaluated using UV spectrophotometry (TU-1901, Puxi Ltd., Beijing, China). The pesticide loading contents ($PLC\%$) of LBPAA were calculated using Eq. 1,

$$PLC\% = (\omega_0 - c \times 0.05 \times 0.1) / M_0 \times 100\% \quad (1)$$

where ω_0 (g) is the pesticide dosage, c (g/L) is the pesticide concentration in the residual liquid, and M_0 (g) is the mass of the dry gel. Paraquat, cyhalofop-butyl, and cyfluthrin were visible by UV detection at 256, 248, and 235 nm, respectively.

Swelling studies

Gravimetric methods were used to measure the swelling behaviors of the hydrogel samples. A sample of each hydrogel (0.10 g) was immersed in deionized water (100 mL) at 25 °C for 24 h to reach swelling equilibrium. The swollen samples were then filtered through 100-mesh gauze and weighed. The equilibrium water absorbency was calculated according to Eq. 2,

$$Q_{eq} = (M - M_0 / M_0) \times 100\% \quad (2)$$

where Q_{eq} (g/g) is the water absorbency calculated per gram of dried sample. M_0 (g) and M (g) are the weights of the dry and swollen samples, respectively.

To study the water absorbency over a range of pH values, a number of acidic and basic solutions were prepared using 0.1 M solutions of HCl and NaOH. The effect of ionic strength of the external solution on water absorbency was investigated in a series of NaCl solutions with concentrations ranging from 1 to 20 mg/L (Liang *et al.* 2009).

Pesticide release kinetics studies

To explore the pesticide release kinetics of LBPAA, the following procedure was followed. Loaded pesticide gels (10 g) were immersed in deionized water (100 mL). At selected times, a sample of each release medium (5 mL) was analyzed by UV spectrophotometry, and a portion of deionized water (5 mL) was added to keep the volume of the release medium constant. The percentage cumulative release (R) of pesticides from the LBPAA gel was calculated according to Eq. 3,

$$R = (M_t + \sum M_{t-1})/M_0 \times 100\% \quad (3)$$

where M_t (g) is the amount of pesticide released at time t and M_{t-1} is the amount of pesticide released at last time. The quantity M_0 (g) is the initial loaded amount of pesticide. Law of pesticide release from LBPAA was studied over a range of pH values and ionic strengths

RESULTS AND DISCUSSION

Composite Morphology

SEM micrographs of PAA and LBPAA composites containing 30, 35, 40, and 45 wt.% lignin are shown in Fig. 1. It can be seen that the network structure of PAA was a closed honeycomb cell (Fig. 1a). With the addition of lignin, the network structure was gradually replaced with a porous structure with a rougher surface morphology. This change in porosity and surface morphology resulted in the composite being able to absorb greater volumes of water than PAA (Chebli *et al.* 2001). The average pore size, channel volume, and specific area also increased upon the addition of lignin up to 40 wt.% (Figs. 1b-1c and Table 1). In addition, when the lignin content was increased to 45 wt.%, the network structure was filled with lignin is too much to hole was closed (Fig. 1e).

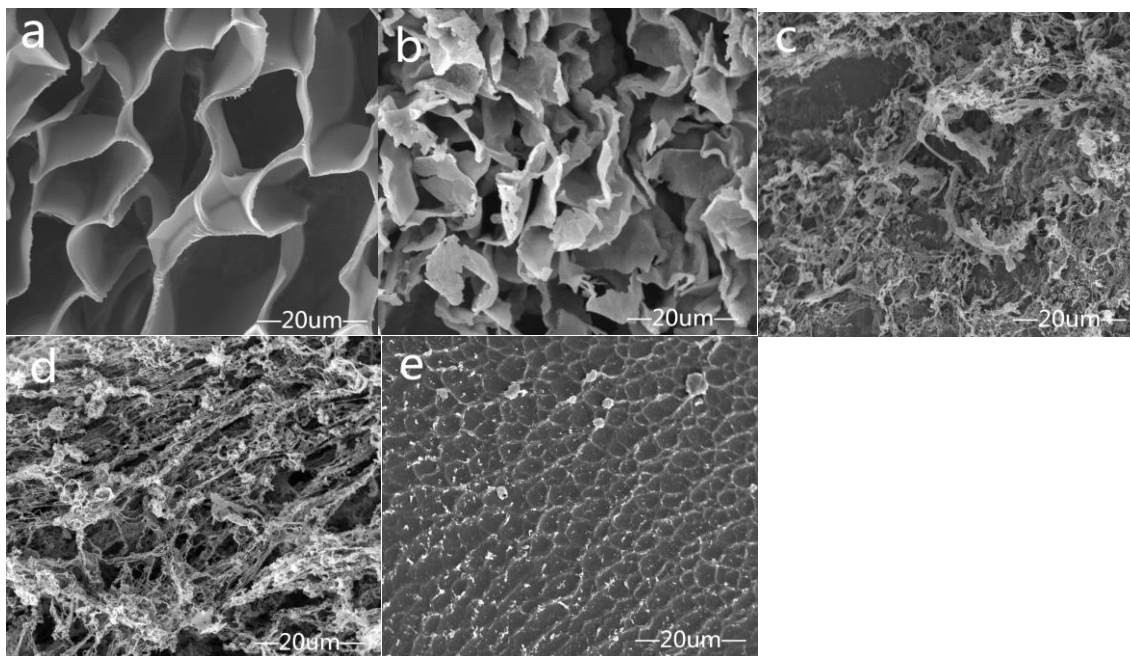


Fig. 1. Scanning electron micrographs of (a) PAA, (b) LBPAA (30 wt.% AL), (c) LBPAA (35 wt.% AL), (d) LBPAA (40 wt.% AL), (e) LBPAA (45 wt.% AL)

Table 1. Pore Characteristics of PAA and LBPA

	Alkali lignin content of LBPA				
	0 (PAA)	30%	35%	40%	45%
Average pore size (r, nm)	-	2.23	3.15	1.86	2.77
Channel volume ($V_g, \text{cm}^3 \cdot \text{g}^{-1}$)	1.5×10^{-4}	1.5×10^{-3}	5.4×10^{-3}	9.7×10^{-3}	1.13×10^{-3}
Specific area ($\text{m}^2 \cdot \text{g}^{-1}$)	0.37	10.11	30.7	122.53	4.15

FTIR of LBPA

FTIR spectroscopy was utilized to study the functional groups of LBPA (40 wt.% lignin) and PAA. The FTIR spectra shown in Fig. 2 confirm the successful preparation of LBPA with the disappearance of the signal at 1743 cm^{-1} corresponding to the ester group. The presence of polyacrylic acid was confirmed by the observation of absorption bands characteristic of carboxyl moieties, at 3432 cm^{-1} (O-H stretching vibration of carboxyl groups) and 1041 cm^{-1} (O-H deformation vibration of carboxyl groups). In addition, as previously mentioned, the signal at 1743 cm^{-1} corresponding to non-dissociated COOH groups in PAA disappeared. This indicated that reaction of lignin and acrylic acid involves the OH and COOH groups (Windeisen and Wegener 2008; Johar *et al.* 2012).

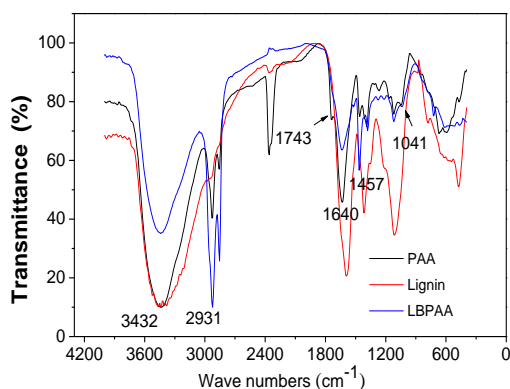


Fig. 2. FT-IR spectra of PAA, lignin, and LBPA

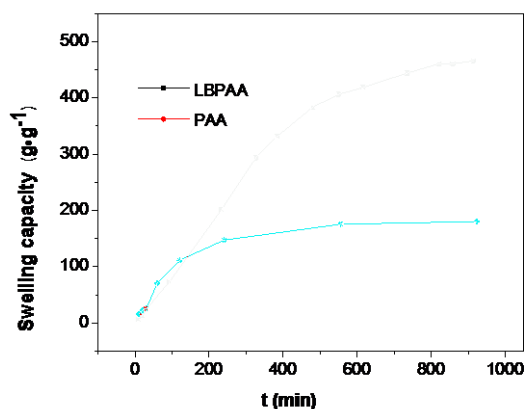


Fig. 3. Swelling capacity of PAA and LBPA in deionized water

Swelling Sensitivity of the Hydrogels

As shown in Fig. 3, the hydrogel swelling equilibrium time of LBPA (40 wt.% lignin) was slower than that of PAA, while the swelling capacity increased to 465 g/g from 180 g/g (Fig. 3). Adsorption capacity of lignin was only 2.54 g/g , far lower than PAA and LBPA, so the adsorption capacity of lignin could be ignored. After the grafting of lignin onto the network structure of PAA, the hydrogel had a higher swelling capacity by the decrease of the density of the network (Fig. 3). A longer swelling time of LBPA is due to the resistance to water from the hydrophobicity of lignin and its filling effect in the network.

Pesticide Loading and Release in Water at $25 \text{ }^\circ\text{C}$

The maximum loadings of three chosen pesticides on PAA and LBPA (40 wt.% lignin) are shown in Fig. 4a, where it is clear that the pesticide loading of LBPA was

greater than that of PAA for all pesticides. The orders of pesticide loading followed the order: cyfluthrin > paraquat > cyhalofop-butyl. It was expected that cyfluthrin could be easily loaded onto PAA and LBPAA, as it contains a number of ether and ester linkages that lead to poor solubility in the dispersion medium (water) (Costa and Sousa Lobo 2001). Paraquat is a water-soluble pesticide. Its strong hydrophilicity makes it easier to interact with the COOH group, so it exhibited a lower loading than cyhalofop-butyl (Singh *et al.* 2008).

The cumulative release rate of pesticides in water at 25 °C from LBPAA and PAA was found to be in the same order of pesticide loading (Fig. 4b). And it can be seen that the release rates of pesticides from LBPAA were found to be rapid. The cumulative release rates after 3 days and 10 days can be seen in Table 2. On the third day, the cumulative release rate of cyfluthrin and paraquat was higher than that of cyhalofop-butyl due to the high load. At the tenth day, as most of the hydrogel was broken, the cyhalofop-butyl's hydrophilicity was the lowest. And the binding force with LBPAA was the lowest, so the release rate increased. In addition, approximately 50% of the pesticide content was trapped within the PAA. Such behavior not only affects the efficiency of the pesticide (higher loading but less delivery), but can also lead to pesticide pollution because of the poor biodegradability of PAA.

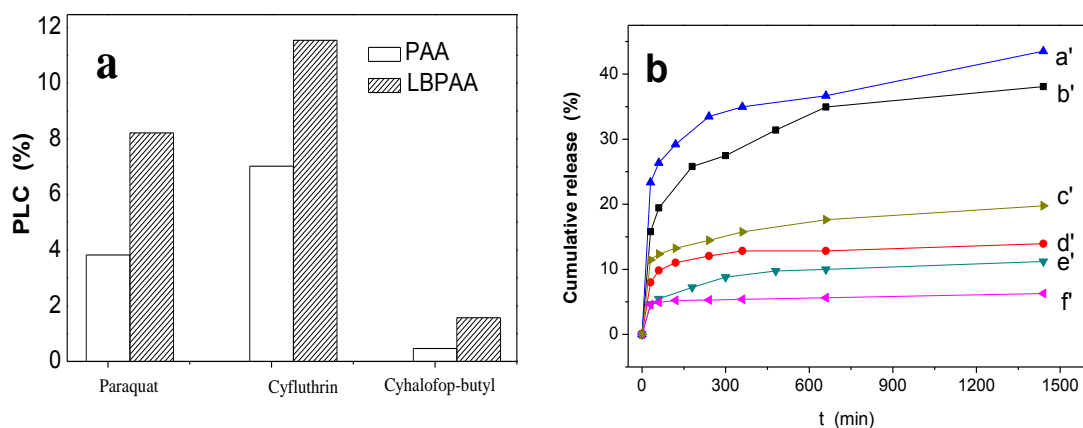


Fig. 4. The loading capacity and cumulative release profiles of PAA and LBPAA: (A) the loading capacities; (B) cumulative release profiles: (a') cyfluthrin released from LBPAA; (b') paraquat released from LBPAA; (c') cyfluthrin released from PAA; (d') cyhalofop-butyl released from LBPAA; (e') paraquat released from PAA; and (f) cyhalofop-butyl released from PAA

Table 2. Cumulative Release Rate of Pesticide Released from Hydrogels

Samples	Pesticides	Cumulative release rate (%)	
		3 days	10 days
PAA	Paraquat	19.5069	58.1531
	Cyfluthrin	29.4076	50.0579
	Cyhalofop-butyl	17.3227	68.4232
LBPAA	Paraquat	54.4952	88.9538
	Cyfluthrin	53.7373	84.2675
	Cyhalofop-butyl	31.3573	91.2284

Effect of pH

Figure 5a shows the response to pH on the water absorbency of the PAA and LBPAA. It was found that both hydrogels exhibited similar swelling behaviors in terms of pH sensitivity. Under acidic conditions (pH 3 to 5 in this study), the majority of carboxylate groups are protonated, thus strengthening the hydrogen bonding interactions between the hydrogel and the water. At high pH ($5 < \text{pH} < 7$), those hydrogen bonds broke, causing a decreasing effect of the H^+ , and the network shrunk in size (pKa of carboxyl group at 4.75). The energy gain from ion association decreased with an increase in the size of ion pairs and the supercollapsed ionomer state became less favorable. At higher pH (7 to 8), the level of deprotonation of the carboxylic groups and the phenolic hydroxyl groups is increased, and so the majority of hydrogen bonding interactions are broken. Under basic conditions ($\text{pH} > 8$), the water absorption capacity of the hydrogel was at a plateau level (Gong *et al.* 2009; Liu *et al.* 2010).

On account of the high cumulative release profiles of cyfluthrin, we selected cyfluthrin for investigation into the effect of pH on the release of pesticides. And solutions of pH 3, 5, and 8 were selected for this study. As can be seen in Fig. 5b, the volumetric expansion (v) of LBPAA follows the order $v_{\text{pH } 5} > v_{\text{pH } 8} > v_{\text{pH } 3}$, and the cumulative release profiles of cyfluthrin followed the same rules. This demonstrates that pH is important not only because of its influence on the structure of the hydrogel network, but also because of its effect on the stability of the pesticide (Ya *et al.* 2011).

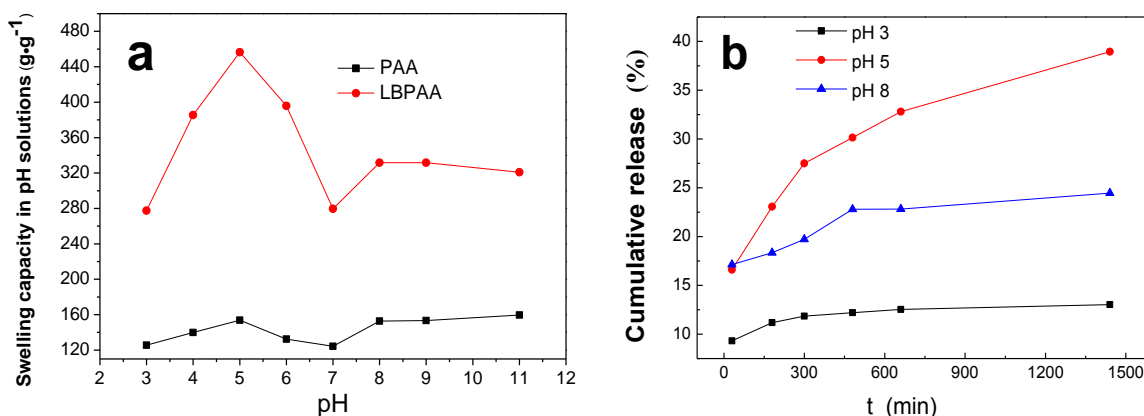


Fig. 5. Effects of pH variation on: (a) swelling capacity of hydrogels; (b) controlled release of cyfluthrin from LBPAA

Effect of Salt Concentration

The effect of the salt concentration of the aqueous solution on the equilibrium swelling and release of cyfluthrin were also studied for the LBPAA hydrogels, as shown in Fig. 6. Compared with PAA, the LBPAA hydrogel was found to have a higher swelling capacity. It was also observed that the hydrogels water absorbency in saline solution reduced significantly upon an increase in NaCl content (Fig. 6a). This was attributed to the presence of both Na^+ and Cl^- ions in solution, resulting in shielding of the electrostatic interactions between opposite charges on the adsorbent surface, thus restricting the spread of a hydrated polymer network. In saline solution, the cumulative release rate of cyfluthrin followed the same trend as the effect of salt ions on water absorption of gel (Fig. 6b).

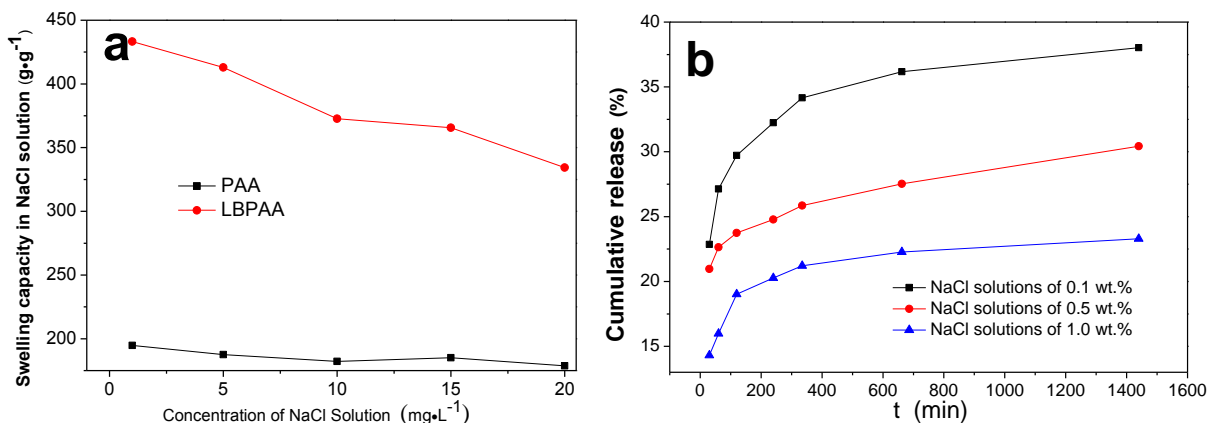


Fig. 6. Effects of varying NaCl content on: (a) swelling capacity of hydrogels; (b) controlled release of cyfluthrin from LBPAA

Release Models and Mechanism

To fully describe the kinetics of the pesticide release process from the controlled release formulations, a range of models and mathematical equations can be applied, as listed in Table 3. The kinetics of cyfluthrin release from both PAA and LBPAA were evaluated according to the Higuchi (Higuchi 1963; Ya *et al.* 2011), Ritger–Peppas (Bayraktar *et al.* 2005; Chakraborty *et al.* 2012), Hixson–Rowell (Siepmann and Peppas 2001), and Baker–Londale (Costa and Sousa Lobo 2001) models.

Based on these estimations, the fit of each model was predicted. The coefficients of determination calculated from four models clearly indicated that cyfluthrin release from PAA and LBPAA could be best described using the Ritger–Peppas and Higuchi models, where the coefficients of determination were greater than 0.9 under all conditions. The n values obtained for our systems suggest that the introduction of lignin to PAA did not result in a change in the diffusion mechanism from that of PAA. This result once again indicates that the lignin moieties are grafted mostly on the surface of the gel network, rather than embedded inside the network.

Table 3. Release Rate Constants of Cyfluthrin from Hydrogels

Release model		PAA	LBPAA
Ritger-Peppas ($\ln Q_t = n \ln t + C$)	n (min^{-1})	0.1397	0.1553
	C (mg/g)	1.9231	2.6324
	R^2	0.9439	0.9905
Higuchi ($Q_t = kt^{0.5} + C$)	k (min^{-1})	0.2597	0.5845
	C (mg/g)	10.4090	22.2990
	R^2	0.9834	0.9517
Hixson-Crowcell ($Q_t^{1/3} = kt + C$)	k (min^{-1})	-2.00×10^{-4}	-6.00×10^{-4}
	C (mg/g)	0.956	0.8992
	R^2	0.8882	0.8569
Baker-Lonsdale ($1.5 - [1 - (1 - Q_t)^{2/3}] - Q_t = kt + C$)	k (min^{-1})	3.00×10^{-5}	1.24×10^{-2}
	C (mg/g)	2.60×10^{-4}	27.3540
	R^2	0.9462	0.8337

In Table 3, Q_t is the amount of pesticide released in time t , n is the Ritger-Peppas release exponent, C is the amount of pesticide in the solution at $t = 0$, and k is the release constant.

CONCLUSIONS

1. A polyacrylic acid lignin hydrogel (LBPAA) was prepared by grafting lignin on the surface of the polyacrylic acid network. Upon grafting, it was observed that the network structure of LBPAA became relaxed, resulting in an increase in water absorbency of the hydrogel.
2. In addition, the LBPAA composite gels were found to be sensitive to pH, temperature, and ionic strength.
3. Finally, the LBPAA demonstrated high loading and sustained release of a range of pesticides, suggesting potential application in controlled pesticide release.

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