

Synthesis and Characterization of Slow-Release Nitrogen Fertilizer with Water Absorbency: Based on Poly(acrylic acid-acrylic amide)/Na-Bentonite

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ABSTRACT: A novel slow-release nitrogen fertilizer with high-water absorbency (SRNFWA) was prepared by cross-linking poly (acrylic acid-acrylic amide)/bentonite and urea. The synthesis conditions were studied systematically and optimized by using the response surface methodology (RSM). Meanwhile, the effects of the concentration of cross-linker, initiator, bentonite, and degree of neutralization of acrylic acid on WA were investigated. The SRNFWA was characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis, and scanning electron microscopy (SEM). The results of SEM showed the undulant and coarse surface, facilitated the permeation of nutrition into the polymeric network. We also investigated the slow release property and release mechanism of the nitrogen from the network structure,

and the WA in different external solutions. The released characteristic of nitrogen was less than 15% by the third day and reached up to almost 75% after 30 days in distilled water. The WA was 700 g g⁻¹ and 150 g g⁻¹ in distilled water and 0.9 wt % NaCl solutions, respectively. These studies exhibited the excellent slow-release property and WA capacity of this polymer in 0.9 wt % NaCl solution and could be quite effective in improving the utilization of fertilizer and its water retention capacity simultaneously. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: slow-release nitrogen fertilizer; clay; functionalization of polymer; response surface methodology; kinetics models

INTRODUCTION

During the second half of the 20th century, the global food production rose to more than double and thus responded to the doubling of world population because of advancement in agricultural technologies. The agricultural production accounted for about 90% of global freshwater consumption during the past century.¹ The manipulation of scarce water resources to irrigate maximum arable land has become a major challenge for farmers and agrarians. Recently, the use of superabsorbent has attracted great attention as a water retaining material for agricultural and horticultural applications.^{2,3}

Superabsorbent polymers are lightly crosslinked with three-dimensional polymer network that has the ability to absorb considerable amounts of water or aqueous fluids in relatively short period of time.^{3–5} But many superabsorbents are based on pure polymers and they are costly and also not preferable to fit for saline-containing water and poor biodegradability in soils, so they are not applicable in many domains of agricultural science.^{6,7} In recent years, the application of new technologies such as adding inorganic clay to the organic-inorganic superabsorbent composites or starch grafting, etc. has changed this state to some extent.^{8–10} Bentonite (a kind of clay) like montmorillonite, beidellite, and nontronite contains a large proportion of expandable clay minerals with a typical 2 : 1 layered structure (smectites). However, the major constituent of the soil is metasilicate, which makes the polymer/bentonite biodegradable. It has a great potential to intercalate with various organic molecules,^{8,11} which may be due to its nanoscale dispersion in the polymer matrix, high aspect ratio of clay platelets and the high cation exchange capacity. In addition, bentonite could make the structure of polymeric network dense and affect the property of the slow release. The clay used in this work was sodium bentonite

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because of its natural abundance in Xinjiang of China, low cost, high cation exchange capacity, and biodegradable properties.

Meanwhile, loss of nitrogen (N) is a serious problem that not only negatively affect environment but also causes economical and resource loss, which could be mitigated by using slow-release fertilizer (SRF).^{7,12} The growth of plants and their quality mainly depend on the quantity of fertilizer and water resource. So, we surmised that the best possible combination of SRF and superabsorbent polymers for improving the nutritional values of plants, mitigating the environmental hazards of water-soluble fertilizers, reducing water evaporation losses, and lowering the frequency of irrigation.^{13,14} Furthermore, it is quite interesting and informative to investigate the synthesis of slow-release nitrogen fertilizer with water-absorbency (SRNFWA) by response surface methodology (RSM) and to characterize for slow-release property and water absorbency (WA) capacity of this polymer.

Keeping in view all these above factors and latest development on water-absorbency materials and SRF, we targeted to prepare a novel SRNF with the good slow-release and water-absorbency properties based on poly (acrylic acid-acrylic amide)/Na-bentonite. First, the influences of the synthesis conditions on the WA were investigated. Second, we selected Box-Behnken Design (BBD) test by using the Design-Expert 7.0 (trial version) for experimental design to measure the efficacy of the SRNF. Finally, the novel SRNFWA synthesized was characterized, and its WA and slow release properties were also determined. Therefore, this study could provide a theoretical guidance for the production of SRNFWA and its potential applications in agriculture and related fields.

MATERIALS AND METHODS

Materials

Acrylic acid (AA, analytically pure, Beijing Chemical Works, Beijing, China) was distilled under reduced pressure to remove the polymerization inhibitor and stored in the brown reagent bottle. Potassium persulfate (KPS) was recrystallized from water. *N*, *N*'-methylene bisacrylamide (NNMBA, purity > 99.9%), urea and acrylamide, cyclohexane, sodium bentonite, sorbitan monostearate (span 60), and all other reagents were all of analytical grade and used directly as received, and all solutions were prepared with distilled water.

Preparation of the SRNFWA

Cyclohexane solution (60 mL, as dispersion medium) was poured into a three-necked, round-bottomed

flask (250 mL), which were equipped with a mechanical stirrer, a reflux condenser, and a thermometer. Then span 60 (1.20 g, as suspending stabilizer) was added into in the solution. The mixture was heated to 40°C and stirred until the surfactant was dissolved completely.

Typically, acrylic acid (5.0 g) was dissolved in the distilled water (20 mL) and was partially neutralized with 4.0 mL of 40 wt % sodium hydroxide solution in an ice bath. Then acrylamide (5.0 g), 1.2 mL NNMBA aqueous solution (0.01 mol L⁻¹), 4 mL of KPS aqueous solution (0.04 mol L⁻¹), sodium bentonite (0.50 g), and urea (5.0 g, as the fertilizer nutrient) were added to the monomer solution and stirred for 30 min until homogenous mixture was obtained. Then the mixture was remixed with the oil phase by stirring at 500 rpm for 30 min to generate the water-in-oil system. When the temperature of mixture was 70°C, the reaction lasted for 3 h. The suspension solution was filtered and the product was dried at 70°C for 12 h. Finally, brown granules of the fertilizer were recovered.

Determination of the WA

WA was measured by the tea-bag method. This method is the most conventional, fast, and suitable for limited amount of samples.^{15,16} The accurately weighted samples ($m_0 = 0.2$ g) were placed into plastic bags (with fine meshes) and the bags were immersed into 500 mL of distilled water and saline solution (0.9 wt % NaCl aqueous solution) to reach the equilibrium swelling at room temperature (25°C), respectively. Then excess solution was removed by hanging the bag until no liquid was dropped off from the gauze. The plastic bags loaded swollen samples were weighed (m_1) and the WA was calculated by Eq. (1).

$$WA = \frac{(m_1 - m_0)}{m_0} \quad (1)$$

Experimental design

After the preliminary study, to obtain high WA and cost control, we selected four factors as the objective of study, examined their interaction, and optimized the experimental program at fixed percentage of cross-linker and initiator by using the RSM, because the RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. Therefore, we used RSM to reduce the number of experimental trials needed to evaluate the multiple experimental parameters and their interactions.^{17,18} So, a four-factor BBD was obtained by using Design-Expert 7.0 (trial version). The WA of the products was evaluated by immersing into the 0.9 wt % NaCl aqueous solution. In

TABLE I
Experimental Design and Results of the BBD Design

Runs	Factors and levels				Responses	
	Neutralization degree of AA (%) X_1	Urea concentration (%) X_2	Bentonite concentration (%) X_3	Reaction time (h) X_4	Experimental	Predicted
1	70	30	15	3	90.96	89.36
2	60	35	15	3	81.08	78.77
3	50	40	15	3	74.98	66.08
4	60	35	15	3	85.71	78.77
5	60	30	15	4	74.69	75.79
6	50	35	15	4	63.39	60.97
7	60	40	10	3	113.77	123.34
8	70	35	20	3	63.83	66.84
9	70	35	15	2	83.51	89.90
10	50	35	15	2	41.94	37.36
11	60	35	15	3	56.33	78.77
12	60	35	20	2	47.56	48.72
13	60	30	20	3	71.82	71.74
14	70	40	15	3	117.04	106.98
15	60	40	15	2	78.35	81.45
16	60	40	20	3	80.24	73.89
17	60	35	10	2	100.34	102.72
18	50	35	20	3	52.62	65.44
19	50	35	10	3	91.98	90.85
20	60	35	10	4	104.00	94.67
21	60	35	15	3	83.00	78.77
22	60	35	15	3	83.10	78.77
23	60	40	15	4	45.19	57.83
24	60	35	20	4	60.33	49.78
25	50	30	15	3	79.83	79.39
26	70	35	10	3	151.26	140.31
27	50	30	15	2	67.62	59.17
28	70	35	15	4	50.74	59.30
29	60	30	10	3	111.71	121.18

general, the response for the quadratic polynomial is described in Eq. (2) by statistic analysis.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j \quad (2)$$

where Y is the predicted response (WA), β_0 is the intercept coefficient, β_i are the linear terms, β_{ii} are the squared terms, β_{ij} are the interaction terms, and X_i and X_j represent the coded independent variables. In this study, the second-order polynomial equation was obtained using the uncoded independent variables such as Eq. (3):

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 \quad (3)$$

Data for Eq. (3) were processed by using the Design-Expert 7.0 program (trial version) and analysis of variance (ANOVA) to estimate the interaction between the process variables and the responses. The set of actual experiments performed (experimental runs 1–29) and predicted results of the WA obtained are shown in Table I. The fit quality of the

polynomial model was expressed by the coefficient of determination R^2 , and its statistical significance was checked by the F test in the same program. All experiments were performed in triplicate.

Measurement of the slow release behavior of SRNFWA

To study the release behavior of the SRNFWA, 0.20 g of SRNFWA was placed into 500 mL of distilled water and 0.9 wt % NaCl aqueous solutions under unstirred condition at 25°C, respectively. Then, 5.0 mL of the solution was taken out to estimate the contents of nitrogen released from the SRNFWA after specific intervals. The amount of released nitrogen was estimated at 430 nm by using UV-Vis spectrophotometer.⁹ All the nitrogen release experiments were performed in triplicate and results were averaged.

To further understand the release process and release mechanism, the release results were analyzed to estimate the value of n and k by using an empirical equation Eq. (4)^{13,19}:

$$M_t/M = kt^n \text{ or } \log(M_t/M) = \log(k) + n \log(t) \quad (4)$$

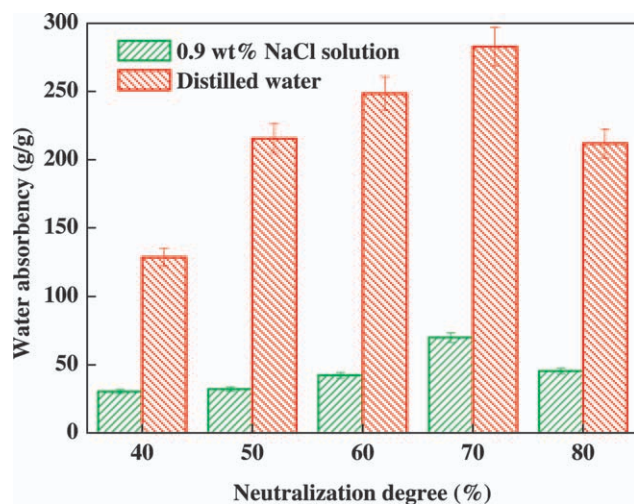


Figure 1 Influence of the neutralization degree on WA: cross-linker 0.06 wt %, initiator 0.6 wt %, bentonite 15 wt %, urea 30 wt %, and reaction time 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where M_t/M is the amount of the released fraction of nitrogen at time (days), n is a release exponent that indicates the release mechanism, and k is a release constant. From the slope and intercept of the plot of $\log(M_t/M)$ versus $\log(t)$, kinetic parameters n and k were calculated.

Characterization of SRNFWA

The infrared spectra of the SRNFWA were recorded on a Fourier transform infrared spectrophotometer (FTIR) (SENSOR27, BRUKER, Germany). The samples were completely dried and grounded to fine powder and blended with KBr.

The surface of the SRNFWA was analyzed by a scanning electron microscopy (SEM) (JSM 740, JEOL; Tokyo, Japan). The samples were dried and the fractions obtained were adhered to sample holders with carbon LIT-C glue. In SEM investigation, the samples were coated with a layer of gold.

RESULTS AND DISCUSSION

Influence of the neutralization degree of AA on WA

The neutralization degree of acrylic acid is defined as the molar percentage of carboxyls in acrylic acid neutralized by NaOH aqueous solution. The WA first increased gradually with the increase of neutralization degree and reached maximum (160 g g^{-1} in distilled water) at 70% neutralization degree and then decreased (Fig. 1). The activity of acrylic acid was found higher than that of acrylate. If the AA could not be neutralized partly, the rate of polymerization was too fast to be control and might result in

the increase of the oligomers. Because these oligomers are water soluble, they have low water absorbance capacity. However, with the increase of the neutralization degree, more carboxylate anions accumulated, and these negative ions would set up an electrostatic repulsion among the network, which caused the expansion of the network and enhanced the WA.¹⁴ As can be observed in Figure 1, the reaction rate decreased and the content of carboxyl groups increased with an increase in neutralization degree up to 70%, showed that an increase in neutralization degree reduced the reaction rate till a certain concentration. This could result in the decrease of the oligomers, hence increased the WA of SRNFWA. This result is in accordance with Liang et al.,¹⁰ who reported that with the increase of neutralization degree, the electrostatic repulsion between the attached carboxylate anions increases, and it could increase the stretching and expansion of the hydrogel network causing an increase in WA.

Influence of the initiator concentration on WA

Initiator concentration is an important parameter for the free radical copolymerization, because it determines the rate of polymerization, molecular weight of the polymer, and monomer conversion. Figure 2 shows the influences of the initiator concentration on WA in 0.9 wt % NaCl solution and in distilled water. The WA of the SRNFWA increased with an increase in the initiator concentration from 0.2 to 0.8 wt % and decreased when the initiator concentration was higher than 0.8 wt %. This is due to the reason that when the initiator concentration was from 0.2 to 0.8 wt %, a very limited amount of free radicals was

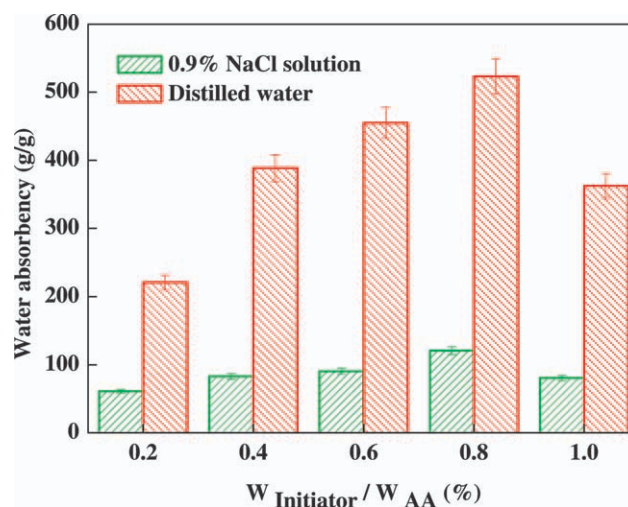


Figure 2 Influence of the initiator concentration on WA: neutralization degree 70%, cross-linker 0.06 wt %, bentonite 15 wt %, urea 30 wt %, and reaction time 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

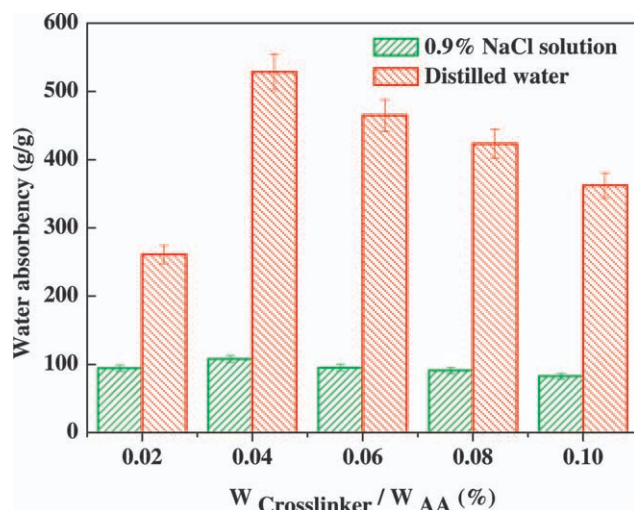


Figure 3 Influence of the cross-linker concentration on WA: neutralization degree 70%, initiator 0.8 wt %, bentonite 15 wt %, urea 30 wt %, and reaction time 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

available that could not accelerate the polymerization reaction at its peak, so the polymerization rate was very slow depicting the low extensiveness and high WA of the system. However, further increase in initiator concentration (>0.8 wt %) increased the cross-linking density, which led to the decrease of the WA.⁷

Influence of the cross-linker concentration on WA

The cross-linker concentration is one of the most important parameters available to control the cross-linking density of the polymer network structure. With the increase of cross-linker concentration, the WA increased and became optimum at 0.04 wt % and above this optimal value, the WA decreased gradually till 0.1 wt % (Fig. 3). The increase in cross-linker concentration up to the optimal value (0.04 wt %) could increase the cross-linking density and decrease the soluble part of the polymer, causing an increase in the WA. When the cross-linker content was higher than 0.04 wt %, the WA decreased. It could be explained on the basis of network water holding capacity as the concentration of cross-linker increases, the cross-linking intensity of the network increases reducing the space among the three-dimensional network for holding water and inhibits penetration of water molecules into the network. Hence, the WA of the SRNFWA exhibited a slow decrease with the increasing cross-linker content. These results are in conformity with the theory of Flory.²⁰

Influence of the Na-bentonite concentration on WA

The effect of Na-bentonite concentration on the WA has been shown in Figure 4. The degree of swelling

reached at maximum level when the concentration of Na-bentonite was 5.0 wt %. This may be due to that Na-bentonite particles serve as the cross-linking points chemically bonded with the monomers,⁸ which could improve the structure of network of the polymer composite. As Liang et al.¹⁰ reported the WA of poly (acrylic acid-co-acrylamide)/kaolin increase with the increase in kaolin content (0–10 wt %). Zhang et al.²¹ also verified the same results and believed that there might be some reaction between bentonite and polymer and analyzed it by IR spectra. Meanwhile, it is worthy to note that the addition of Na-bentonite could reduce the cost of the product. When the concentration of Na-bentonite was above 5.0 wt %, a large number of monomers were embedded by the Na-bentonite, which might alter the elastic response of the structure of polymeric network and could restrict the diffusion of small substances (such as H₂O, Na⁺, etc.) into the polymer network and consequently reducing the WA. As Liang et al.¹⁰ described that when the excess clay was dispersed in the polymer, the clay acted as non-reactive filler, which contributed to the decrease of WA of the polymer.

Optimization by RSM

The predicted values of design matrix and experimental results of the SRNFWA have been presented in Table I. The obtained results were, then, subjected to the RSM to evaluate the relationship between the degree of neutralization of AA (X_1), urea concentration (X_2), Na-bentonite concentration (X_3), and reaction time (X_4). The second-order polynomial model for the WA fitted in terms of the coded factors as follows:

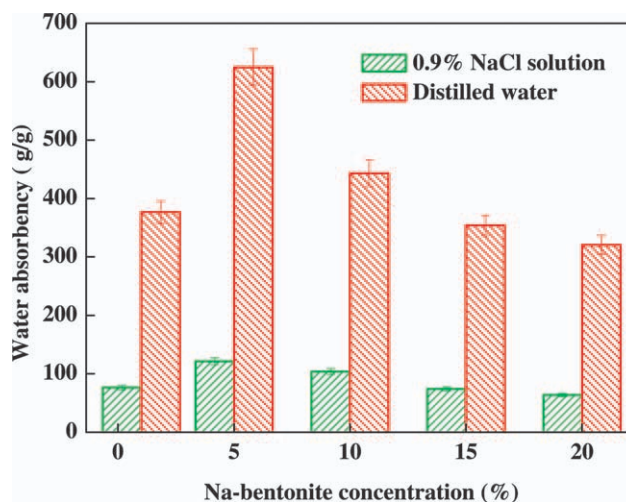


Figure 4 Influence of the Na-bentonite concentration on WA: neutralization degree 70%, initiator 0.8 wt %, cross-linker 0.04 wt %, bentonite 15 wt %, urea 30 wt %, and reaction time 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
ANOVA Results for the Quadratic Equation Proposed by Design-Expert 7.0 for WA

Source	Sum of squares	Degree of freedom	Mean square	F	P > F	
Model	4743.02	14	338.79	8.14	0.0002	Significant
Residual	582.40	14	41.60			
Lack of fit	397.63	10	39.76	0.86	0.6163	Not significant
Pure error	184.77	4	46.19			
Total	5325.43	28				
Adjusted R ² 0.7813			Predicted R ² 0.5157			
R ² = 0.8906			Adequate precision = 12.428			

$$Y = 43.59 + 7.12X_1 + 0.60X_2 - 13.84X_3 - 0.98X_4 + 4.33X_1X_2 - 6.73X_1X_3 - 7.59X_1X_4 + 0.89X_2X_3 - 5.63X_2X_4 + 1.28X_3X_4 + 0.80X_1^2 + 3.89X_2^2 + 6.92X_3^2 - 9.30X_4^2 (R^2 = 0.8906, P = 0.0002) \quad (5)$$

The statistical significance of the second-order model equation was evaluated using ANOVA (Table II). The coefficient of determination ($R^2 = 0.8906$) and the Prob > F value ($P = 0.0002$) for Eq. (5) indicated that the second-order polynomial model fitted the experimental results better. The model F value of 8.14 and a low probability value ($P > F = 0.0002$) implied that the model is significant for the WA in 0.9 wt % NaCl solution. There is only a 0.02% chance that a model F value of this large could occur due to noise. The lack of fit F value of 0.86 indicated that lack of fit for the model was not significant. But there was a significant difference between the predicted R^2 (0.5157) and adjusted R^2 (0.7813). These differences indicated a large block effect or some other possible problems with the model. So, the model needed to be modified by removing the statistically non-significant terms (X_3X_4 , X_1^2 , and X_2X_3 , the P values not shown) to get a new regression equation^{22,23}[Eq. (6)]:

$$Y = 44.11 + 7.12X_1 + 0.60X_2 - 13.84X_3 - 0.98X_4 + 4.3X_1X_2 - 6.73X_1X_3 - 7.59X_1X_4 - 5.63X_2X_4 + 3.74X_2^2 + 6.77X_3^2 - 9.45X_4^2 (R^2 = 0.8880, P < 0.0001) \quad (6)$$

Comparing eqs. (6) and (7), the regression coefficient R^2 of 0.8880 was decreased. According to Jogle-

kar and May²⁴ and Wu et al.,²⁵ for a good fit of a model, the correlation coefficient should be at a minimum of 0.80. High R^2 value illustrates good agreement between the calculated and observed results within the range of experiment. So the regression coefficient indicates the probability and feasibility of experimental results. The ANOVA table of the fitted model (Table III) indicated that the regression was highly significant ($P < 0.0001$), although the lack of fit F value of 0.69 implied the lack of fit of model was not significant relative to the pure error. The P value ($P = 0.7295$) was higher than that in the unmodified model ($P = 0.6163$). The predicted R^2 of 0.6473 was in reasonable agreement with the adjusted R^2 of 0.8156. The "Adequate precision" ratio of the model was 15.132 (Adequate precision > 4), which was an adequate signal for the model. It indicated that this modified model can be used to navigate the designed space. All these results showed that the designed model was fit better for the process than the unmodified model [Eq. (5)].

The predicted versus observed values of WA have been given in Figure 5. The observed points on the plot revealed that the observed experimental values were found relatively near to the straight line and showed satisfactory correlation among these values ($r = 0.9423$).

Interactive effect of the four factors

The WA of the SRNFWA over different combinations of independent variables was visualized through three-dimensional view of response surface

TABLE III
ANOVA Results for the Quadratic Equation Proposed by Design-Expert 7.0 for WA

Source	Sum of squares	Degree of freedom	Mean square	F	P > F	
Model	4729.15	11	429.92	12.26	<0.0001	Significant
Residual	596.27	17	35.07			
Lack of fit	411.50	13	31.65	0.69	0.7295	Not significant
Pure error	184.77	4	46.19			
Total	5325.43	28				
Adjusted R ² 0.8156			Predicted R ² 0.6473			
R ² = 0.8880			Adequate precision = 15.132			

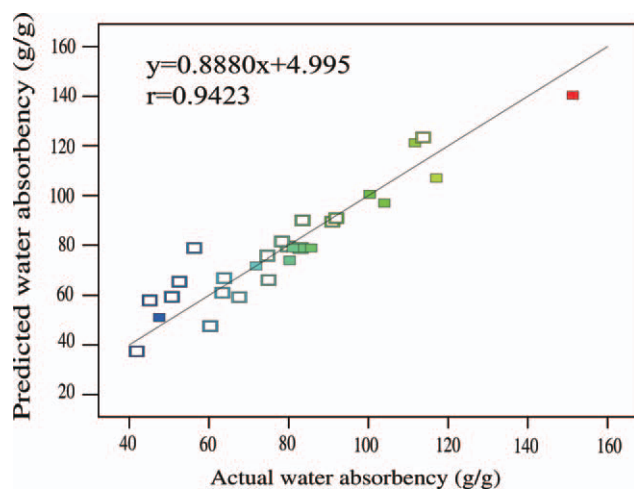


Figure 5 Comparison plot between the experimental and model predicted water adsorption capacity (the data point symbolize the experimental runs 1–29). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

plots (Fig. 6). It indicated the interaction between neutralization degree and urea concentration on WA of SRNFWA in 0.9 wt % NaCl solution. It can be observed that the WA increased gradually with the increase of urea concentration and neutralization degree. As can be seen from Figure 6(a), the maximum WA was obtained at 70% neutralization degree and urea concentration of 40 wt %. When neutralization degree kept at a constant value within the range of 50–70%, the WA increased from 66 g g⁻¹ to 86 g g⁻¹ with the increase of the amount of urea from 30 to 40 wt %. However, when urea concentration was a constant value within the range of 30–40%, the WA increased from 66 g g⁻¹ to 100 g g⁻¹ with the increase of neutralization degree from 50–70%. So the neutralization degree could have a more positive effect on WA than urea concentration.

It can be seen from the Figure 6(b) that when neutralization degree kept at a constant value within the range of 50–70%, the WA increased with the decrease of the amount of bentonite from 20 to 10

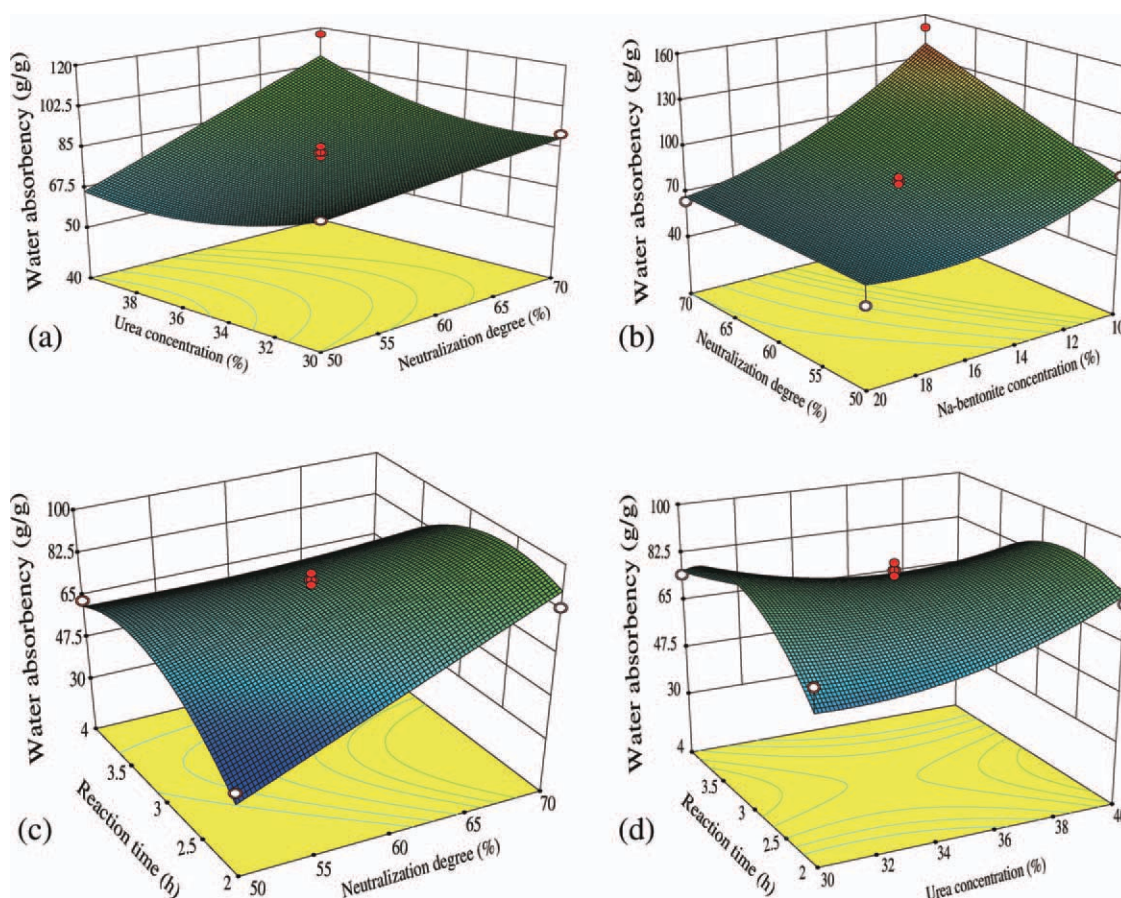


Figure 6 (a) 3-D response surface: interactive effect of the neutralization degree and urea concentration at reaction time 3 h and bentonite concentration 15 wt %. (b) 3-D response surface: interactive effect of the neutralization degree and bentonite concentration at urea concentration 35 wt % and reaction time 3 h. (c) 3-D response surface: interactive effect of the neutralization degree and reaction time at urea concentration 35 wt % and bentonite concentration 15 wt %. (d) 3-D response surface: interactive effect of the urea concentration and reaction time at neutralization degree 60% and bentonite concentration 15 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

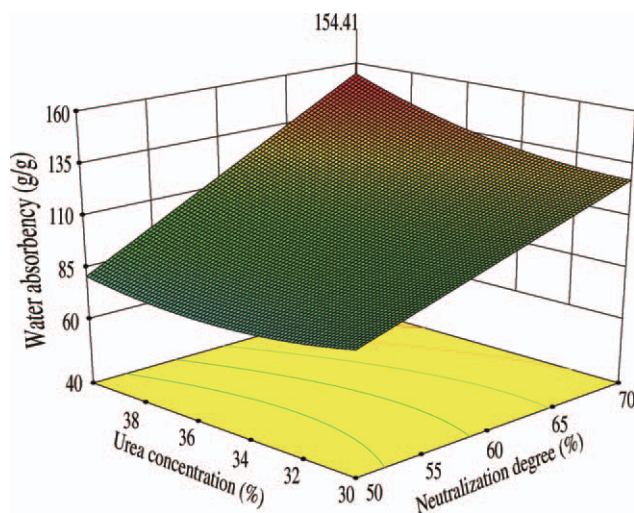


Figure 7 3-D response surface optimized: degree of neutralization 68.46%, cross-linker 0.04 wt %, initiator 0.8 wt %, bentonite 10.10 wt %, urea 39.91 wt %, and reaction time 2.18 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wt %. The largest increment observed was 75 g g^{-1} (65 g g^{-1} to 140 g g^{-1}). When bentonite concentration maintained at a constant value of 10–20%, the WA also increased with the increase of neutralization degree from 50 to 70 wt %. However, the maximum increment found was only 52 g g^{-1} (88 g g^{-1} to 140 g g^{-1}). Therefore, this phenomenon might indicate that the bentonite concentration could have a more positive effect on WA than neutralization degree.

From the Figure 6(c) and (d), we can notice that the WA increased at the beginning, reached to the maximum level and then reduced with the reaction proceeded. But there were some marked differences in the Figure 6(c) and (d). In the Figure 6(c), the WA of the samples reached the maximum level, within shorter period of time with the increase of neutralization degree. This could indicate that the neutralization degree could determine the reaction time to some extent. It's worth noting that the contour of the Figure 6(d) presented an elliptic characteristic with the long axis of the ellipse running along the urea concentration axis in some range of urea concentration (30–35% and 35–40%, w/w). This could predict that the reaction time has greater impact on the absorbance capability than urea content.²³

It can be seen from the response surface maps (Fig. 6) that the interaction terms imparted different effects on WA, and we could determine the following preliminary conclusion: bentonite concentration > neutralization degree > reaction time > urea concentration. According to this conclusion, we may control the polymerization process by adjusting the amount of various parameters. Hence, the optimum parameters were determined by keeping in view the

cost effectiveness of process and all concerned operational conditions. As shown in Figure 7, the maximum WA of 152.8 g g^{-1} was predicted at optimum conditions: reaction time 2.18 h, neutralization degree 68.46%, the cross-linker, initiator, bentonite, and urea concentrations of 0.04 wt %, 0.8 wt %, 10.10 wt %, and 39.91 wt %, respectively. To confirm the predicted values, a series of experiments were performed under the optimum conditions. An average WA of 150 g g^{-1} was obtained experimentally, which was close to the predicted value.

Swelling behavior of the SRNFWA in distilled water and 0.9 wt % NaCl solution

The dynamic swelling behavior was also studied in distilled water and 0.9 wt % NaCl solutions because external stimuli such as ionic strength, temperature, or solvent composition could change the swelling ability and structure of polymer.²⁶ Figure 8 depicted the swelling kinetics curves of the SRF in 0.9 wt % NaCl solution and distilled water. It can be seen that the swelling behavior of polymer in both solutions was similar, i.e., the initial swelling stage of the SRNFWA in 0.9 wt % NaCl solution and the distilled water was very fast during first 300 min, then followed by a gradual swelling until the equilibrium was attained after about 400 min, indicating the maximum WA of the SRNFWA after immersing in both 0.9 wt % NaCl solution and the distilled water.

However, the swelling rate and WA of the fertilizer in the distilled water were higher than 0.9 wt % NaCl solution. It might be due to the difference in ionic concentration and osmotic pressure.^{21,27} According to the Floy-Rehner theory, the osmotic pressure of a hydrogel during swelling comes partly from the pressures caused by the nonuniform distribution of mobile counter ions between the gel and the external

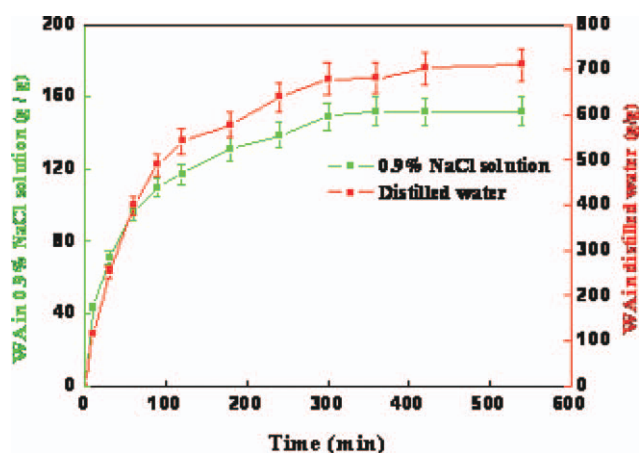


Figure 8 Swelling kinetics of the SRNFWA in 0.9 wt % NaCl solution and distilled water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

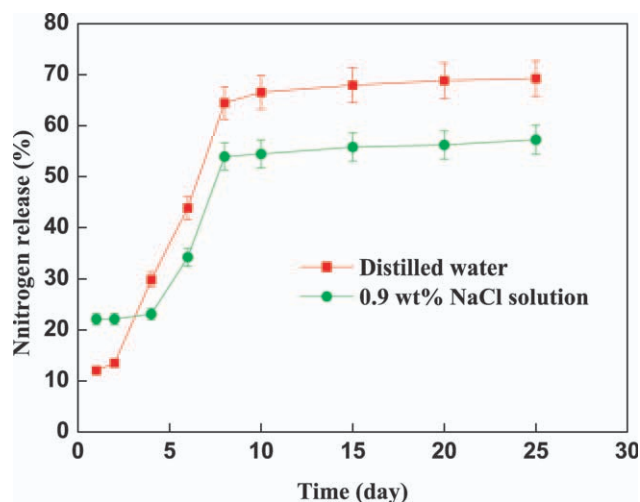


Figure 9 Release behaviors of nitrogen from the SRNFWA in distilled water and 0.9 wt % NaCl solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution.^{20,28} When the external solution is distilled water, the mobile ions (NH_4^+ , Na^+) remain inside the hydrogel to neutralize the fixed charges on the network chains, which maintain the electroneutrality condition of the swollen hydrogel. When the external solution is the salt solution, ions diffuse from the solution into the network. Although the total concentration of the mobile ions in the hydrogel was higher than initial value, the concentration difference between inside and outside the hydrogel would reduce. As a result, the osmotic pressure decreased, and the WA in 0.9 wt % NaCl solution was found lower than that of distilled water.

Slow-release behavior of nitrogen from the SRNFWA

The SRNFWA was tested for its slow-release properties under optimum conditions in distilled water and 0.9 wt % NaCl solution at room temperature. The samples in different media exhibited similar release kinetics curves comprised of three stages as shown in Figure 9. The first stage included the slow release of nitrogen during first 3 days, followed by its faster release in the second stage from 5 to 10 day and at last stage began to level off after 15 days. At the first stage, the nitrogen released from SRNFWA was 13.49 and 23.11% in the distilled water and 0.9 wt % NaCl solutions, respectively. In the second stage, the SRNFWA showed a faster release rate (slope of the graph). When the SRNFWA was placed into the water, it absorbed water, swelled, and became to the hydrogel. Then a dynamic exchange would occur between the free water in the hydrogel and the water in the distilled water or salt solution. So the urea encapsulated in

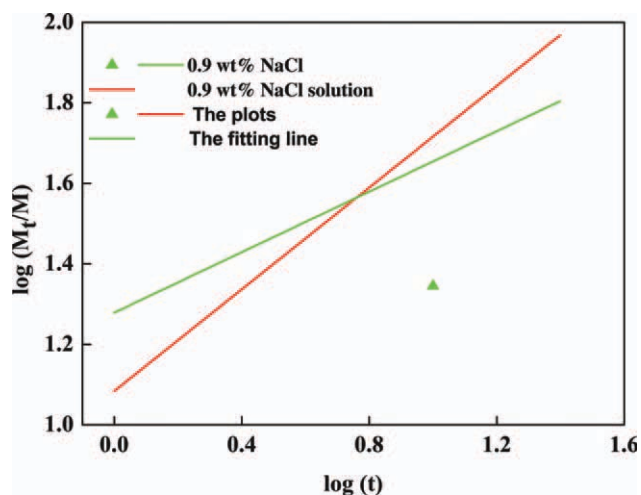


Figure 10 The linear plots of log release fractions of nitrogen against log time in distilled water and 0.9 wt % NaCl solution.

the hydrogel network would diffuse out of the network structure through this dynamic water exchange. The final stage displayed a gentle slow-release curve showing the attainment of equilibrium stage between the hydrogel and the solution.

The n value is an empirical parameter characterizing the release mechanism.^{13,29} On the basis of the diffusion exponent, an n value of 0.5 indicates the nutrient release mechanism approaches to Fickian diffusion; whereas n equal to 1.0 indicates the nutrient release mechanism approaches to zero-order release. The n value from 0.5 to 1.0 is a nutrient release mechanism for non-Fickian diffusion. As shown in Figure 10, the plots of $\log(M_t/M)$ versus $\log(t)$ exhibited a straight line with good linear correlation coefficient (Table IV). By fitting experimental data using Eq. (4), the values of the release exponent n and kinetic constants k in the different media can be calculated through the slope and intercept of the above lines. The values of k , n , and R^2 (correlative coefficients following linear regression) of the SRNFWA were calculated. The n values were 0.63, and 0.38 in the distilled water and 0.9 wt % NaCl solution, respectively. According to the n values, we could determine the nitrogen release mechanism by non-Fickian diffusion or chain relaxation control release in distilled water and it could be controlled by a combination of diffusion from the network and degradation of the SRNFWA.^{29,30} However, the

TABLE IV
The k , n , and R^2 for N Release from SRNFWA in Different Medium

External solution	n	k	R^2
Distilled water	0.63	12.02	0.88
0.9 wt % NaCl solution	0.38	19.05	0.80

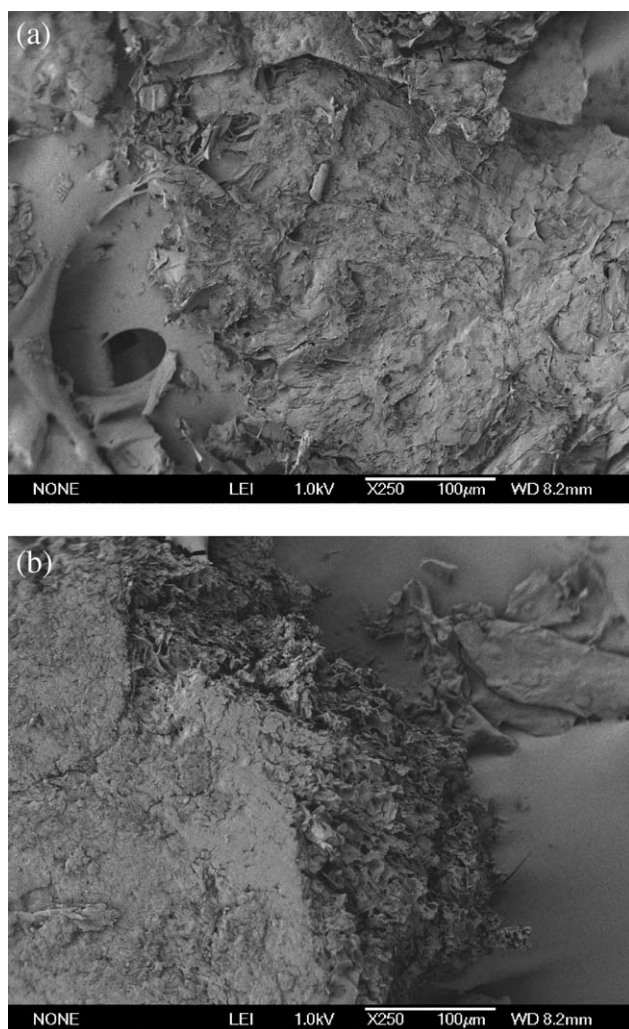


Figure 11 (a) SEM micrographs of the surface of the SRNFWA. (b) SEM micrographs of cross-section of the SRNFWA. The linear plots of log release fractions of nitrogen against log time in distilled water and 0.9 wt % NaCl solution.

n value was 0.38 in 0.9 wt % NaCl solution, which might be due to the osmotic pressure caused by the sodium ions. Therefore, there might have different release mechanisms when the SRNFWA dipped in different media.

Structure and characteristics of the SRNFWA

The micrographs of the surface and cross-section of the SRNFWA have been shown in Figure 11. In the Figure 11(a), the SEM results showed a well dispersion of the clay particles in SRNFWA matrix. Therefore, sodium bentonite could be a good substrate for SRNFWA. It could be observed that cross-linked AA/AM/bentonite-urea displayed the coarse surface, which greatly increased the contact area of the water and polymer, and facilitated the permeation of water into the polymeric network. As shown in the

Figure 11(b), the SRNFWA formed a more intact porous network structure, which allowed extremely fast absorption of water into the matrix of SRNFWA. These results supported the fact that the SRNFWA exhibited a faster swelling rate and excellent WA (Fig. 8) regardless of whether the external solution was 0.9 wt % NaCl solution or distilled water. Mudiyansele and Neckers³¹ also reported that increase in porosity could enhance the swelling rate of polymer material.

FTIR analysis of SRNFWA, urea, and bentonite

Figure 12 showed the FTIR spectra of Na-bentonite (a), urea (b), and poly (AA-co-AM)/Na-B/urea (c), respectively. The FTIR spectrum of the urea displayed the characteristic carbonyl peak at 1623 cm^{-1} (C=O), and two N–H absorbency bands at 3442 and 3348 cm^{-1} .³² However, the two peaks became smaller in Figure 12(c), showing the involvement of –CONH₂ group from urea in the reaction system. The spectrum of the Na-bentonite mainly peaks characteristic at 1037 cm^{-1} correspond to the Si–O stretching, and at 915, 3624, and 3442 cm^{-1} correspond to the OH group. The three absorption peaks of OH group on Na-bentonite disappeared after the reaction compared with Figure 12(a) and (c). However, the Si–O stretching still existed in the Figure 12(c). It might be due to the grafted polymerization between –OH groups on bentonite and monomers occurred during the reaction course.^{10,21} Santiago et al.⁸ also reported the similar conclusion that hydroxyl groups on the surface of bentonite would react with the carboxyl group of poly (SA). So, Na-bentonite particles could be acted as cross-link points developed some sort of bonding with the polymer.

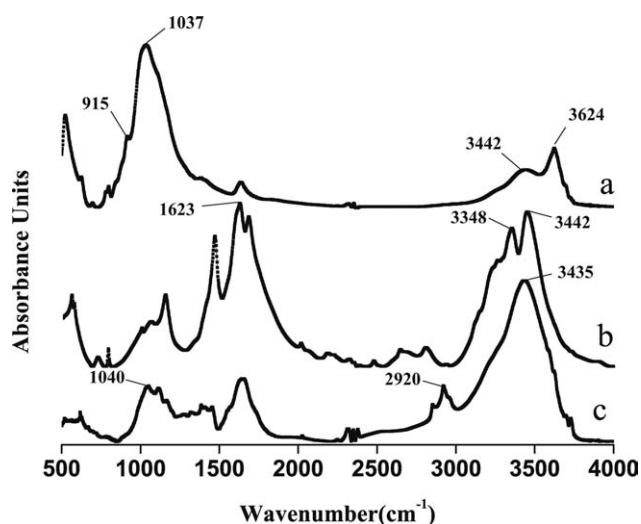


Figure 12 FTIR spectra of Na-bentonite (a), urea (b), and SRNFWA (c).

CONCLUSIONS

A novel SRNFWA based on cross-linked poly (AA-co-AM)/bentonite and encapsulated urea was synthesized by inverse suspension polymerization. RSM was applied successfully for the optimization of operational conditions to improve the WA and reduce production cost. The optimum values for neutralization degree, cross-linker concentration, initiator concentration, bentonite concentration, urea concentration, and reaction time were found to be 68.46%, 0.04 wt %, 0.8 wt %, 10.10 wt %, 39.91 wt %, and 2.18 h. The SRNFWA were characterized by UV, FTIR, SEM, and elemental analysis. The WA of the SRNFWA was 700 g g⁻¹ in distilled water and 150 g g⁻¹ in 0.9 wt % NaCl solution. Elemental analysis results showed that the nitrogen contents of the SRNFWA was 16.95%. The SRNFWA exhibited excellent WA and slow release properties, and the nitrogen released could not exceed 70% after 28 days. All these results provide theoretical guidance for the practical applications of this SRNFWA in many fields of agriculture science.

References

- Shiklomanov, I. A.; Institute, S. H.; Petersburg, S. *Water Int* 2000, 25, 11.
- Huttermann, A.; Orikiran, L.; Agaba, H. *Clean-Soil Air Water* 2009, 37, 517.
- Puoci, F.; Iemma, F.; Spizzirri, U. G.; Cirillo, G.; Curcio, M.; Picci, N. *Am J Agr Biol Sci* 2008, 3, 299.
- Omidian, H.; Rocca, J. G.; Park, K. *J Control Release* 2005, 102, 3.
- Chen, J.; Park, H.; Park, K. *J Biomed Mater Res* 1999, 44, 53.
- Wu, L.; Liu, M. Z. *Polym Adv Technol* 2008, 19, 785.
- Xie, L. H.; Liu, M. Z.; Ni, B.; Zhang, X.; Wang, Y. F. *Chem Eng J* 2011, 167, 342.
- Santiago, F.; Mucientes, A. E.; Osorio, M.; Rivera, C. *Eur Polym J* 2007, 43, 1.
- Chen, L.; Xie, Z. G.; Zhuang, X. L.; Chen, X. S.; Jing, X. B. *Carbohydr Polym* 2008, 72, 342.
- Liang, R.; Liu, M. Z.; Wu, L. *React Funct Polym* 2007, 67, 769.
- Bulut, Y.; Akcay, G.; Elma, D.; Serhatli, E. *J Hazard Mater* 2009, 171, 717.
- Fan, X. H.; Li, Y. C. *Soil Soc Sci Am J* 2010, 74, 1635.
- Wu, L.; Liu, M. Z. *Carbohydr Polym* 2008, 72, 240.
- Khan, S.; Hanjra, M. A. *Food Policy* 2009, 34, 130.
- Zohuriaan-Mehr, M. J.; Kabiri, K. *Iran Polym J* 2008, 17, 451.
- Mohamadnia, Z.; Zohuriaan-Mehr, M. J.; Kabiri, K.; Razavi-Nouri, M. *J Polym Res* 2008, 15, 173.
- Chen, M. J.; Chen, K. N.; Lin, C. W. *J Food Eng* 2005, 68, 471.
- Karacan, F.; Ozden, U.; Karacan, S. *Appl Therm Eng* 2007, 27, 1212.
- Al-Zahrani, S. M. *Int J Eng Sci* 1999, 37, 1299.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- Zhang, J.; Yuan, K.; Wang, Y. P.; Gu, S. J.; Zhang, S. T. *Mater Lett* 2007, 61, 316.
- Aktas, N.; Boyaci, I. H.; Mutlu, M.; Tanyolac, A. *Bioresour Technol* 2006, 97, 2252.
- Chou, K. W.; Norli, I.; Anees, A. *Bioresour Technol* 2010, 101, 8616.
- Joglekar, A. M.; May, A. T. *Cereal Food World* 1987, 32, 857.
- Wu, Y. Y.; Zhou, S. Q.; Qin, F. H.; Ye, X. Y.; Zheng, K. *J Hazard Mater* 2010, 180, 456.
- Hua, S.; Wang, A. *Carbohydr Polym* 2009, 75, 79.
- Horkay, F.; Tasaki, I.; Basser, P. J. *Biomacromolecules* 2000, 1, 84.
- Okay, O.; Sariisik, S. B. *Eur Polym J* 2000, 36, 393.
- Shaviv, A. *Adv Agro* 2000, 71, 1.
- Wu, L.; Liu, M. Z. *Ind Eng Chem Res* 2007, 46, 6494.
- Mudiyanselage, T. K.; Neckers, D. C. *J Polym Sci Pol Chem* 2008, 46, 1357.
- Ni, B.; Liu, M. Z.; Lü, S. Y. *Chem Eng J* 2009, 155, 892.