

The Hydrolysis Kinetics of Kitchen Waste and Each of Its Components in Sequencing Batch Anaerobic Digestion

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(Received: 09 January 2014; accepted: 18 March 2014)

With zero- and first-order kinetics, the hydrolysis and gas production process during the batch anaerobic digestion of single components and mixed kitchen waste were analyzed. It was found that in the single-component system, the zero-order kinetic and first-order kinetic fitting results were close, with a coefficient of correlation R^2 of 0.95. The descending of the tested components by their hydrolysis and gas-production speed was proteins > starches > celluloses > lipids, and the hydrolysis constants k for the components were correspondingly 0.0366, 0.0331, 0.0215, and 0.0154. The zero- and first-order kinetic fitting results were close. The gas production process had some proportional relationship with the hydrolysis process, but had no obvious relationship with the acid-production acidogenesis process. For mixed kitchen wastes, the four-component first-order kinetics model, which considers the multiple components being hydrolyzed separately with different hydrolysis constants k , had the best fitting effect; the coefficient of correlation R^2 was over 0.95. The kinetic fitting effects of the other models, the zero-order kinetics and the single-component first-order kinetics which treats the mixture as a whole with a common hydrolysis characteristics and the $k = 0.02$, as well as the two-component first-order kinetics which divided the mixture into rapid hydrolysis and slow hydrolysis groups, were all not ideal.

Key words: Multiple components; Gas production; The first-order kinetics; kinetic fitting.

The hydrolysis of particulate organic material is a complex process, which is described with mainly three types of particle hydrolysis models: particle concentration-based models, particle surface area-based models, and particle component-based models. The most commonly used models are the ones based on the concentration of particles, such as first-order kinetic model, Contois model and two-phase model¹⁻³. However, these classic models have their

own limitations. The first-order kinetic model is generally believed an accumulated experience expression and unsuitable for describing the digestion of material with high solid content. The Contois model cannot well explain the influence of temperature on hydrolysis rate. The two-phase model, on the other hand, involves too many parameters. In addition, these models all treat an organic mixture as a whole with common hydrolysis character, despite the difference in the hydrolyses of different components. Yasui.H pointed out that in the anaerobic digestion process of an organic mixture, different components may be hydrolyzed separately according to their respective hydrolysis constants K^4 .

The first-order kinetic model is the easiest and most practical hydrolysis model; it has been

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adopted by the anaerobic digestion model No.1 (ADM1) of the international water association⁵. In this study, the hydrolysis and gas production in batch anaerobic digestion of single component and kitchen waste mixture were fitted with zero- and first-order kinetics to study the digestion of kitchen waste. The diffusion and mass transfer during digestion were ignored⁶⁻⁷.

Materials and Methodology

Experimental Materials

The kitchen wastes for the experiments were collected from the residential area of Shenyang Northern Hospital, and cut into pieces in diameters of 1-2 mm or 3-4 mm as two groups of experimental materials. The sludge was from Northern Sewage treatment Plant of Shenyang, and had been domesticated. The main physical and chemical parameters of the mixture of kitchen waste and the inoculum are shown in Table 1.

EXPERIMENTAL

The reactor for the experiments consisted of two wide-mouth bottles (1L) that acted as the fermentation tank and the gas collector respectively, and a volumetric flask (1L) as the water collector. The bottles were sealed with rubber stoppers and sealant and connected with the glass tube and anti-aging latex tube. Air tightness was ensured when the device was connected. An automatic constant-temperature water bath thermostat was employed as the heating device.

Methodology and instrumentation

In the single-component digestion experiments, egg white, rice, minced fat and lettuce were used as the fermentation materials to represent proteins, starches, lipids and celluloses, respectively. One reactor was used for each fermentation material, with 50 g of the dried material and 300 ml of sludge added in the fermentation tank.

The mixed kitchen waste experiments included anaerobic digestions of the two groups of mixtures in different diameters as described in section 1.1 were used. Fifteen parallel samples from each group were used. Each fermentation tank was added 100 g of dried kitchen waste and 300 ml of sludge, and then water to increase the volume to 1L. The fermentation lasted for 36 days at 37°C. Fermentation broths were measured every 2-3 days,

Table 1. Characteristics of different samples material

Component	TS %	VS/%	VS/g
Starches	48	91.73	44.03
Celluloses	28	84.07	23.54
Lipids	13	73.45	9.55
Proteins	11	81.32	8.95
Inoculum		60.81	

Table 2. Fitting parameters of single-component

	R ² /zero	slope	R ² /first	k
Proteins	0.973	246.28	0.958	0.0366
Starches	0.972	238.42	0.959	0.0331
Lipids	0.951	176.17	0.883	0.0154
Celluloses	0.979	125.75	0.962	0.0215

Table 3. Gas production parameters of single component

Component	Initial VS/g	digestive VS/g	gas production potential mL*gVS ⁻¹
Proteins	40.66	26.67	237.8
Starches	45.87	28.13	217.8
Lipids	36.73	14.78	303.9
Celluloses	42.04	19.95	159.7

Table 4. Fitting parameters of VS,TS

Fitting	R ² (4mm)	R ² (2mm)
TS	0.986	0.991
VS	0.98	0.981

Table 5. Fitting parameters of accumulative gas production of mixed kitchen wastes

Fitting	R ² (4mm)	R ² (2mm)
Zero-order	0.904	0.901
1-first-order	0.892	0.884
2-first-order	0.857	0.863
4-first-order	0.978	0.974

Table 6. Fitting parameters of earlier stage of mixed kitchen wastes

Fitting	R ² (4mm)	k/slope
Zero-order/4mm	0.941	0.939
1-first-order/4mm	0.781	
Zero-order /2mm	0.939	
1-first-order/2mm	0.794	

and the corresponding fermentation tank was removed after measurement.

The total solids (TS) and volatile solids (VS) were measured by drying at 103 ~ 105°C and 600 !. The pH was measured by a digital pH meter, gas was collected by drainage method, and the components of the fermented liquid were measured through Shimadzu LC-10A HPLC detection .

Single-component kitchen waste digestion experiment

Establishment of the kinetic model

The kinetic reaction can be expressed as:

$$-\frac{dC}{dt} = KC \quad \dots(2.1)$$

In the formula, K is the hydrolysis constant (d-1) and C is the volatile solids content, (g VS). Integrating Eq. (2.1) and we can get

$$C = C_0 e^{-Kt} \quad \dots(2.2)$$

where C_0 is the initial volatile solids concentration(g VS).

The degree of hydrolysis of a material can be represented by the accumulative gas production. Simplifying the whole gas production process, the gas production rate equation can be expressed as follows:

$$\frac{dG}{dt} = -\alpha \frac{dC}{dt} \quad \dots(2.3)$$

In the formula, $\frac{dG}{dt}$ is the gas production rate (mL·d⁻¹)during reaction, and α is the volatile conversion rate of gas production (mL · g⁻¹VS).

Integrating Eq. (2.3) and substituting it in Eq. (2.2), we can obtain:

$$G = G_0 + \alpha C_0 (1 - e^{-Kt}) \quad \dots(2.4)$$

In the formula, G is the cumulative gas production at the time (mL) and G_0 is the initial

accumulative gas production (mL).

In the batch anaerobic digestion, G_0 was 0, thus Eq. (2.4) can be simplified as:

$$G = \alpha C_0 (1 - e^{-Kt}) \quad \dots(2.5)$$

Eq. (2.5) is then the simplified kinetic model for the anaerobic digestion of kitchen waste⁸⁻¹⁰.

Kinetic fitting for single component

Through the zero- and first-order kinetic fitting of the accumulative gas production of single-component kitchen waste, it was deduced from the curve slope and hydrolysis constant k that by descending order of their hydrolysis rate and gas-producing speed^[11], the tested components should be in the order proteins > starches > celluloses > lipids, the values of k were correspondingly 0.0366 and 0.0331, 0.0215, and 0.0154 d⁻¹ for the four components. Most of the fitting coefficients of correlation R² were greater than 0.95, showing a good correlation. The only exception was for lipids, and it is attributable to the slower degradation of lipid in the early stage than the other components^[12].

Digestion of mixed kitchen wastes

Experimental results

As Fig.4 shows, in the first four days, the gas production was normal. During the period from the 5th day to the 10th day, gas production was very low, pH<5.0, and VFA concentration of the fermented liquid was around 3000 mg/L. During the period from the 10th day to the 20th day, gas production gradually increased to the maximum, pH increased to over 6.0, and VFA concentration gradually reduced to below 1500 mg/L. After 20 days, both the gas-producing rate and the pH reduced gradually, and the VFA concentration increased. After the 30th day of experiment, gas ground to a halt.

Relationship between hydrolysis and gas production

As seen in Figs. 3 and 4, a linear relationship existed between the hydrolysis of TS and VS and the accumulative gas production process; the value of R² was over 0.98.

Relationship between acidogenesis and gas production

As Fig.4 shows, the accumulative gas production did not have a specific relationship with the acetic acid content and VFA concentration,

Table 7. Fitting parameters of later stage of mixed kitchen wastes

Fitting	R ² (4mm)	R ² (2mm)
Zero-order	0.721	0.713
1-first-order	0.801	0.81
2-first-order	0.813	0.805
4-first-order	0.971	0.968

suggesting an unobvious relationship between the gas production process and the acid production process.

As Fig.5 shows, gas production rate

increased with increasing acetic acid content with occasional fluctuations, yet a clear linear relationship was not observed.

As Fig.6 shows, at pH < 6.5, acetic acid

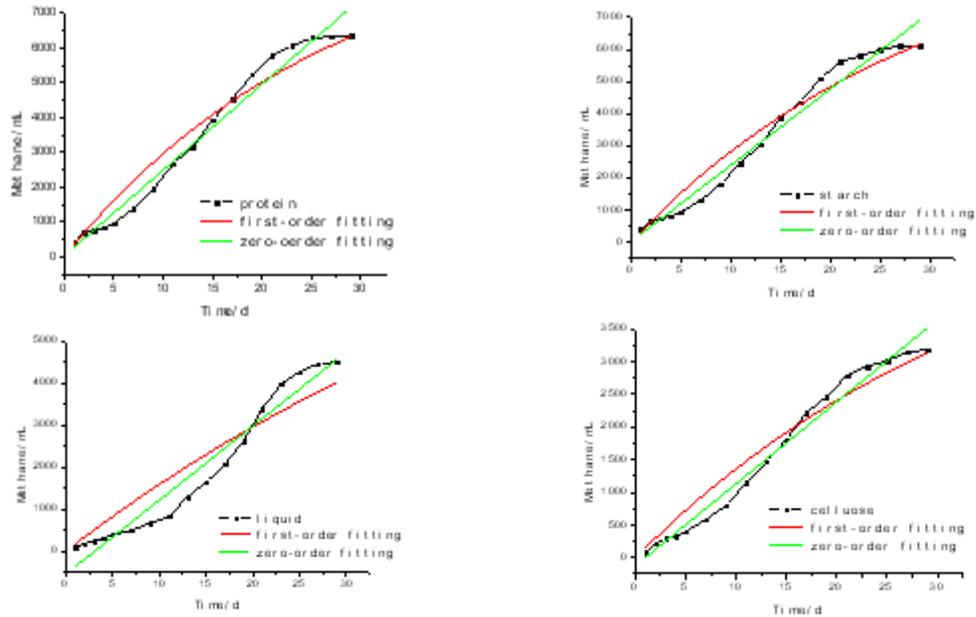


Fig. 1. Fitting curves of cumulative gas production of single-component

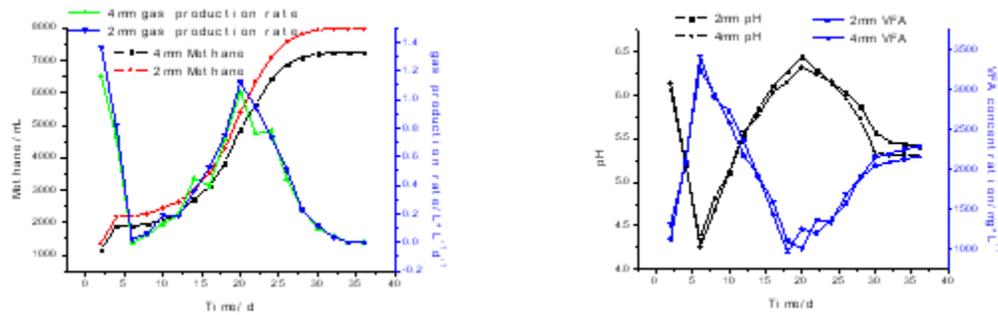


Fig. 2. Experimental results of mixed Kitchen waste

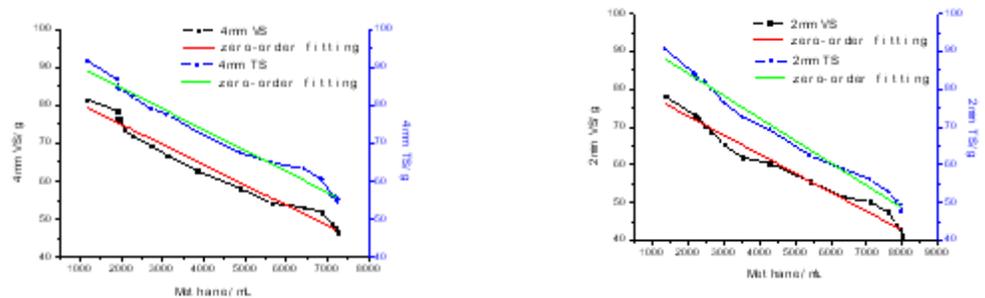


Fig 3. The relationship between VS, TS and accumulative gas production

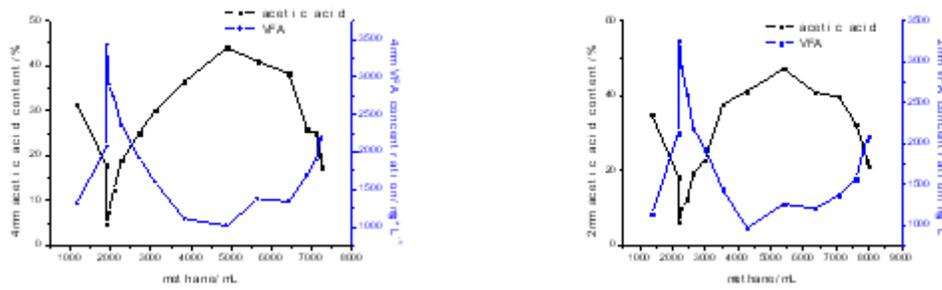


Fig. 4. The relationship between gas production and acetic acid content, VFA

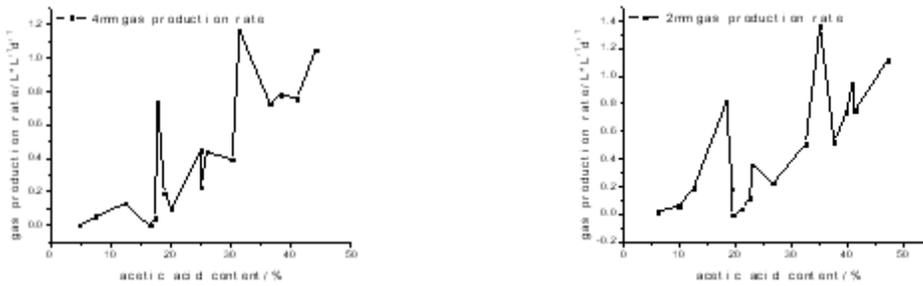


Fig. 5. Impact of acetic acid content on gas production rate

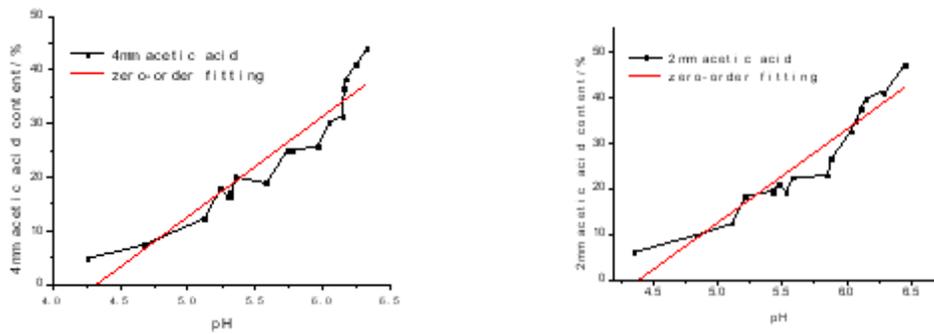


Fig. 6. Impact of pH on acetic acid content

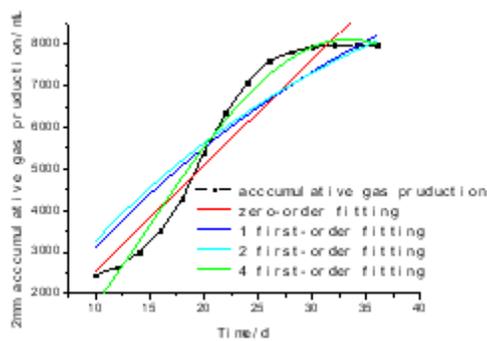


Fig. 7. Fitting equation of accumulative gas production of mixed kitchen wastes

content increased with increasing pH, except for occasional fluctuations. A low linear relationship was exhibited.

Kinetic analysis

Establishment of the kinetic model for the multi-component system

As the first-order kinetic model does not include the demurrage period, the kinetic fitting of accumulative gas production was done for the fermentation from the 10th or 12th day, when the gas production resumed. Organic wastes can be divided into rapid hydrolysis group and slow hydrolysis group, according to the composition of the mixed kitchen wastes. The proportions of starches and celluloses were respectively 48% and 28%, higher than those of proteins and lipids, which

were 11% and 13%, respectively. Therefore, the mixed kitchen waste was simply treated as a two-component mixture of starches and celluloses, which are hydrolyzed with different hydrolysis constants k . The two-component first-order kinetics equation is $y = a * 53 * 217.8 * (1 - e^{-0.0331 * x}) + (1 - a) * 33 * 159.7 * (1 - e^{-0.0214 * x})$. To study the different digestive characteristics of different components in the system, the multi-component first-order model was established according to the content of each component. The four-component first-order kinetics equation is $y = a * 44.03 * 217.8 * (1 - e^{-0.0331 * x}) + b * 8.95 * 237.8 * (1 - e^{-0.0366 * x}) + c * 159.7 * 33 * (1 - e^{-0.0214 * x}) + (1 - a - b - c) * 9.55 * 303.9 * (1 - e^{-0.0154 * x})$ ^{[13][14]}.

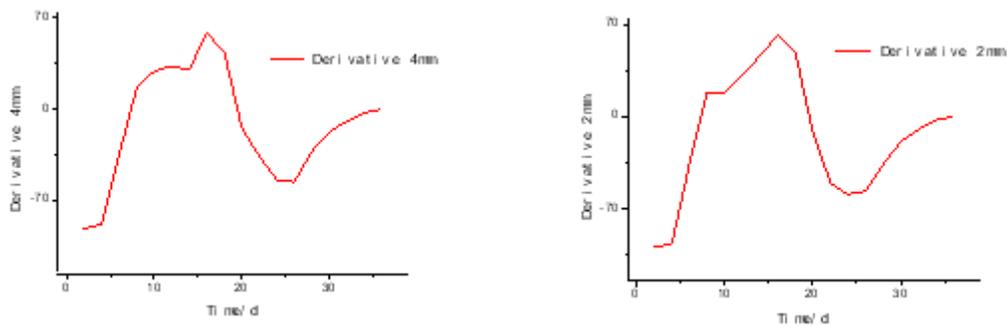


Fig. 8. Derivative of accumulative gas production of mixed kitchen wastes

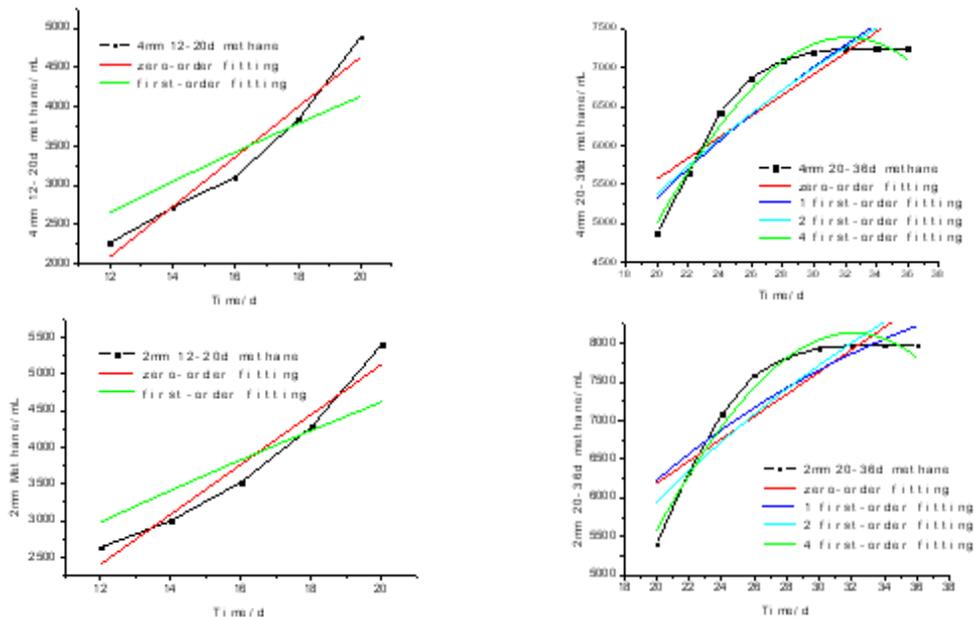


Fig. 9. Fitting of different period of accumulative gas production of mixed kitchen wastes

For mixed kitchen wastes, the 4-component first-order model, which considers the multiple components being hydrolyzed separately with different value of k , had the best fitting effect; the coefficient of correlation R^2 was over 0.95. The kinetic fitting effects of other models, the zero-order kinetics and the single-component first-order model which treats the mixture as a whole with a common hydrolysis characteristics and $k = 0.02d^{-1}$, as well as the two-component first-order kinetics model which divided the mixture into rapid hydrolysis and slow hydrolysis groups, were all not ideal.

Kinetic fitting of the accumulative gas production of mixed kitchen wastes

Generally, gas productions from proteins and starches were faster than those from celluloses and lipids. In addition, one material may have different gas production rates in different stages. According to the change of gas production rate, the anaerobic digestion process was divided into two stages: earlier stage and later stage^[15].

Through 2-order derivative, the point where the concavity and convexity of the gas production curve changed and 2-order derivative was 0 was identified and taken as the boundary of the earlier and later stages. According to the 2-order derivative, this point appeared on the 20th day, thus the period between the 12th and 20th days and the period after the 20th day were defined as the earlier stage and the later stage of fermentation, respectively.

For the later stage of gas production, the 4-component first-order model had the best fitting effect; the coefficient of correlation R^2 was over 0.95. The other three models, the zero-order kinetics model, the single-component first-order model, and the two-component first-order model, all had unsatisfying kinetic fitting effects.

Throughout all the diagrams, there was no significant difference between the changes of the hydrolysis and gas production of the kitchen waste mixture groups with particle sizes of 2 mm and 4mm, and the hydrolysis constants were close. This observation indicates that particle size is not a major influencing factor of the hydrolysis constant k . At $pH < 5.0$, the VFA concentration was above 2500 mg/L and the process of hydrolysis and gas production nearly stopped, indicating that the hydrolysis constant k was

restrained in the condition. The TS content was 5% in the single-component fermentation experiment and 10% in the mixture fermentation experiment, and the fitting coefficients of correlation were over 0.95 for both experiment. Such results indicate that the first-order hydrolysis kinetics model is suitable for the digestion of material with low substrate concentration.

CONCLUSIONS

1. In single-component systems, the descending of the tested components by their hydrolysis and gas-production speed was proteins > starches > celluloses > lipids, and the hydrolysis constants k for the components were correspondingly 0.0366, 0.0331, 0.0215, and 0.0154. The zero- and first-order kinetic fitting results were close.
2. The gas production process had some proportional relationship with the hydrolysis process, but had no obvious relationship with the acid-production acidogenesis process.
3. For mixed kitchen wastes, the four-component first-order kinetics model, which considers the multiple components being hydrolyzed separately with different hydrolysis constants k , had the best fitting effect; the coefficient of correlation R^2 was over 0.95. The kinetic fitting effects of the other models, the zero-order kinetics and the single-component first-order kinetics which treats the mixture as a whole with a common hydrolysis characteristics and the $k = 0.02$, as well as the two-component first-order kinetics which divided the mixture into rapid hydrolysis and slow hydrolysis groups, were all not ideal.

ACKNOWLEDGEMENTS

This work was supported by the National science and technology support. (No. 2012BAC25B07)

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