Adsorption-desorption of K^+ and its availability of variable charge soil and permanent charge soil in central southern China

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1. Introduction

- Since the 1970, potassium deficiency symptoms on various crops began to be reported from some areas in central southern China. As one of the most important problems in agricultural production, the study of the effects of K application on crops was started.

- In this area, experimental results showed:

  1) Effect of K application on the yield increasing and quality improvement for main crops were significant when adequate N, P fertilizers were applied and balanced fertilization with other nutrients.

  2) Rational K application depended on different cropping systems and the optimum K application rate determination was according to soil-K supplying capacity.

- In view of soil-K supplying capacity being closely related to its charge and surface characters, particularly K^+ adsorption-desorption, fixation characters and its availability in soil, but they were obviously different between variable charge soil and permanent charge soil.
- On the basis of field and lab experimental results, the adsorption-desorption characters and availability of K^+ in variable charge soil (Ultisol) and permanent charge soil (Entisol) in central southern China were summarized as follows.

2. General properties of soil tested and composition of its clay.

2.1. General chemical properties of soils tested

The difference of general chemical properties of testing variable charge soil (1) and permanent charge soil (2) in central southern China are listed in table 1.

Table 1. The general chemical properties of soils tested

Soil type	pH (H_2O)	Free $CaCO_3$ (%)	OM (%)	BS (%)	CEC (cmol/kg)
1 (Ultisol)	4.85 (26)*	0 (26)	1.56 (6)	15.47 (30)	10.78 (30)
2 (Entisol)	7.72 (11)	0.538 (4)	2.53 (10)	100 (10)	28.8 (10)

* Number of soil samples.

2.2 Compositions of soil clay are listed in table 2

Table 2. Chemical and mineral composition of soil clay

Soil type	K_2O (%)	CaO (%)	MgO (%)	SiO_2/Al_2O_3	SiO_2/R_2O_3	Clay mineral composition (%)
1	1.717 (23)*	0.076 (23)	0.755 (23)	2.214 (25)	1.835 (25)	Kaol. Illi. 1.4 nm interg. Verm 40 39 20 few
2	4.477 (3)	0.427 (3)	3.863 (3)	3.23 (3)	2.42 (3)	Illi. Verm Kao. Mont. Chlo. 52 30 16 few trace

*…Number of soil samples. Kao-Kaolinte, illi.- -Illite, 1.4nm interg…1.4nm intergrade,Verm,… vermiculite, Mont….Montmorillonite, chlo.—chlorite.

3. The adsorption-desorption characters and availability of K^+ in soils tested

The variable charge soil and permanent charge soil used in the experiments were redoxic paddy soil derived from Ultisol and albic paddy soil derived from Entisol (gray fluvo-aquic soil), respectively.

3.1 Results

3.1.1 Adsorption curves of K^+ in testing soils with application of N, P, K fertilizers (Fig. 1)

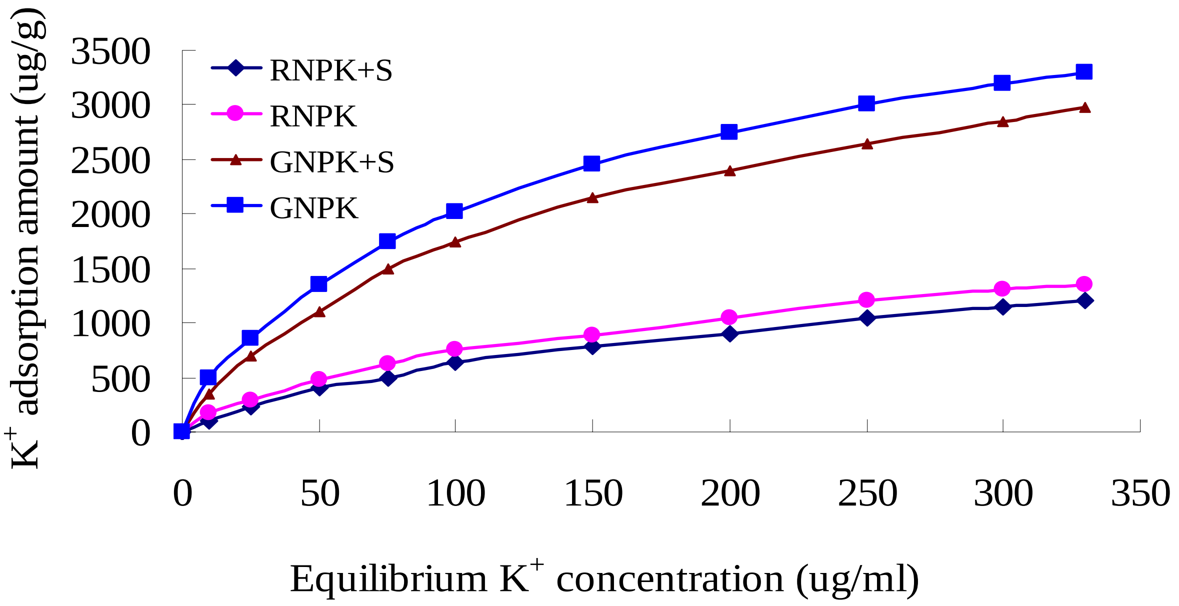

Fig. 1 Adsorption isotherm curves of K^+ for the soils tested

- Fig.1 showed that the amount of K^+ adsorbed by soils increased with increasing K^+ concentration in the equilibrium solution. Under the same concentration of K^+ in the equilibrium solution, the amount of K^+ adsorbed by permanent charge soil was obviously more than that of variable charge soil. For example, when the concentration of K^+ added was 400 μ g/ml, the amount of K^+ sorbed by permanent charge soil (3032 μ g/g) was 1.28 times higher than that (1332 μ g/g) of variable charge soil.

3.1.2 The adsorption kinetic experiment results of K^+ in soil tested (Fig. 2) presented that :

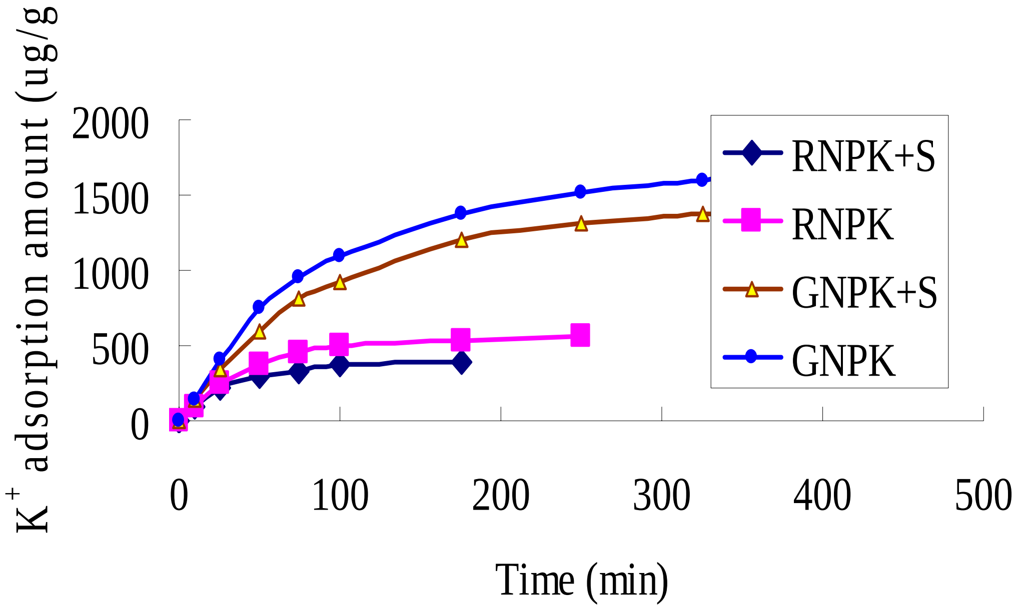

Fig.2. The change of adsorption amount of K^+ in soils tested with time goes on

the maximum adsorption amount of K^+ accumulated in permanent charge soil (1904 μ g/g) was 2.07 times more than that in variable charge soil (621 μ g/g).

3.1.3 From the curves shown in Fig. 3, we can see that the adsorption speed of K^+ in the initial 20-30 minutes stage of adsorption reaction for soils tested did not have obviously difference.

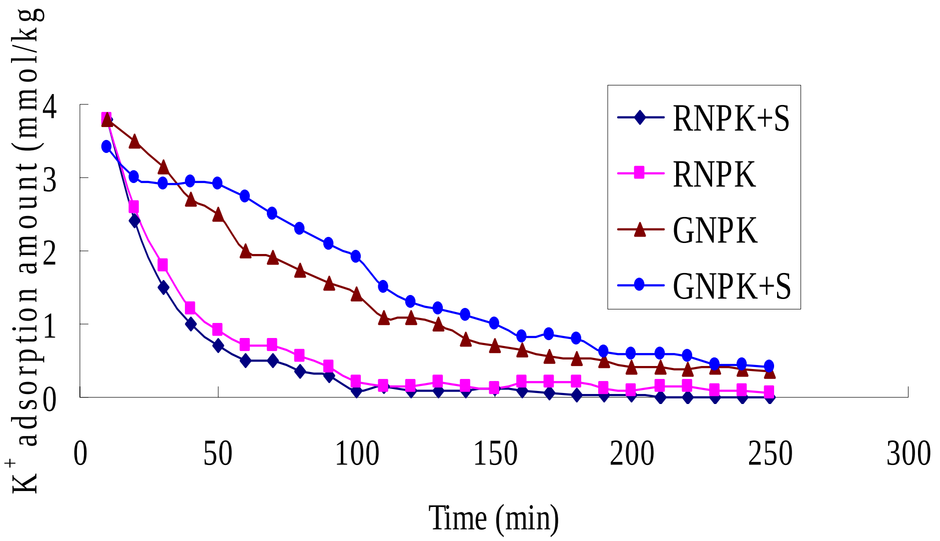

Fig.3. The adsorption amount of K^+ in soils tested on an unit time with the change of time.

But the difference were more and more remarkable with extension the reaction time, and the adsorption speed of K^+ in permanent charge soil was far exceed than that in variable charge soil.

3.1.4 The curves in Fig. 4 indicated that the desorption rate of K^+ sorbed by variable charge soil was the greatest.

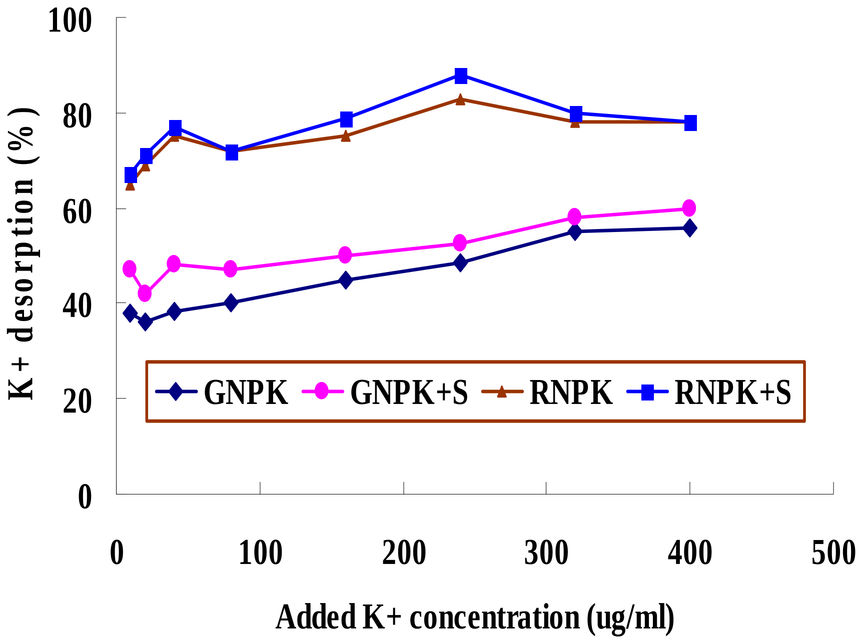

Fig.4. The desorption rate curves of K+ sorbed by soils tested.

This implied the K+ of adsorption form in variable charge soil was easy to desorb and it in permanent charge soil was hard to desorb.

3.2 Analysis and discussion

- The differences of the adsorption-desorption characters and availability of K^+ in both variable charge soil and permanent charge soil were directly related to their clay mineral composition. From table 2 we can see: kaolinite (40%) and illite (30%) are the main clay minerals in the variable charge soil while illite (52%) and vermiculite (30%) are the main clay minerals in the permanent charge soil.

3.2.1 **Kaolinite** is 1:1-type mineral, which structure consists of a unite (a single 0.7 nm layer) made up of one tetrahedral and one octahedral sheet. The surface area of kaolinite is about 7-30 m^2/g and consists largely of external planar surface and edge surface. The 1:1 layer has little or no permanent charge because of the low amount of isomorphous substitution in either the tetrahedral or octahedral sheets. Consequently, the CEC is low (about 3-15 cmol/kg). The content of K fixed, sorbed-desorbed are very low.

3.2.2 illite, vermiculite, montmorillonite, chlorite and 1.4 nm intergrade mineral are 2:1-type minerals. The structure consists of two tetrahedral sheets bound to either side of an octahedral sheet.

3.2.2.1 Illite

Illite is derived from the weathering of mica and its octahedral sheet is dioctahedral. The charge amount of per unit illite is 0.6-1.0. the interlayer charge is balanced by K^+ and the interlayer K^+ is nonexchangeable. Therefore, the layers of illite are nonexpansible and can not fix K^+. Its specific surface is about 70-120 m^2/g and the predominance one is external surface. Consequently, the CEC of illite only has 10-40 cmol/Kg. Illite is thought to differ from muscovite primarity in having poor crystallinity, lower K^+ content and higher H_2O content.

3.2.2.2 vermiculite

- Vermiculite usually formed by the alteration of a mica, trioctahedral vermiculite in soil may be formed by alteration of biotite, phlogopite or chlorite. Its octahedral sheet carries a positive charge of 0.1 to 0.9 and the tetrahedral sheet has a negative charge of 0.9 to 1.4, resulting in a total negative charge of 0.5 to 1.0. The charge deficiency is balanced by exchangeable cations (usually Mg^{2+}, sometimes accompanced by small amount of Ca^{2+}) located between the 2:1 layer. The specific surface is internal surface is relatively larger (600-800 m^2/g) and the predominant surface is internal surface. Consequently, the CEC of vermiculite is about 100-150 cmol/kg, and most originate from interlayer sites, only a few originate from external surface.

A double layer of H_2O molecules is located in the interlayer space, giving vermiculite its 1.4 nm basal spacing and limited expansibility. Interlayer H_2O layers facilitated both the easy migration of cations in interlayer space and the easy of ion exchange. In ion exchange reactions, involving vermiculite and ion pairs form Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Na^{+} or Li^{+}, complete exchange of the sorbed ion by the counter ion is easily accomplished.

Particularly, the high charge per formula unit gives vermiculite a high CEC and causes them to have a high affinity for weakly hydrated cations such as K^{+}, NH^{4+} and Cs^{+}. Fixation of K^{+} was caused by the close fit within the hexagonal cavities in tetradehal sheets of vermiculite, so, it also can be significant in soils high in vermiculite.

3.2.2.3 Montmorillinite

- The interlayer cation of Montmorillinite is Ca^{2+}, Mg^{2+}, Na^{+}, etc. exchangeable cations but not K^{+}. The layer binding force is weak molecular bond, the basal spacing ranged 1.0-1.7 nm. The charge amount of per unit is 0.2-0.6 in which 80% come from isomorphic substitution and 20% come from edge surface broken bond. The specific surface is about 700-800 m^2/g. Its expansibility and shrinkability is much strong. The fixing power for K^{+} is weaker.

3.2.2.4 Chlorite

- Chlorite minerals have a 2:1 layer structure with an excess of negative charge balanced by a positively charged interlayer hydroxide sheet rather than K^+. The summation of the 2:1 layer and the interlayer hydroxide sheet results in a chlorite layer having a thickness of about 1.4 nm. The CEC of chlorite is relatively small (about 10-40 cmol/Kg) and the specific surface is about 70-150 m^2/g.

3.2.2.5 1.4 nm intergrade mineral

- The combination of a 2:1 layer with hydroxy-Al in the interlayer of vermiculite and smectite give a structure similar to that of chlorite. The interlayer hydroxy-Al is not exchangeable. The CEC is lower than that of vermiculite or smectite. Hydroxy-Al interlayer in 2:1 clay minerals can significantly influence the ion exchange behavior of K^+, NH_4^+, Cs^+, Rb^+ and can provent their fixation also.

4 The effect of returning straw to the field on adsorption-desorption characters and availability of K^+ in testing soils

4.1 Results

Fig. 1 showed that:

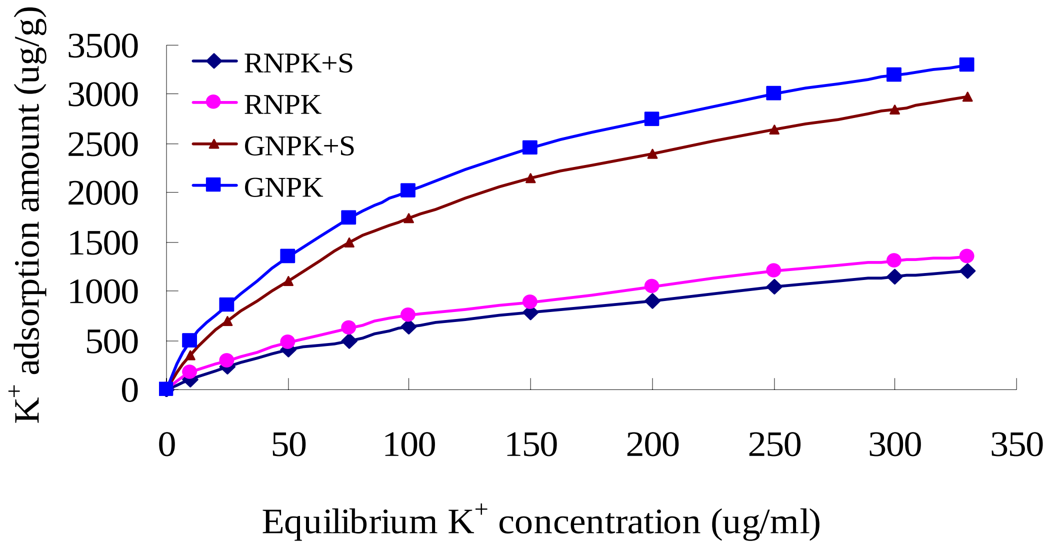

Fig. 1 Adsorption isotherm curves of K^+ for the soils tested

1) K^+ adsorption amount of soils tested was no obvious difference between the treatment of returning straw to the field cooperated with the application of N, P, K fertilizers (RNPKS or GNPKS) and the treatment only application N, P, K fertilizers (RNPK or GNPK), when K^+ concentration in equilibrium solution for variable charge soil and permanent charge soil was < 50 μ g/ml and <10 μ g/ml, respectively.

2) the difference between them would change to distinct with increasing k^+ concentration within a certain range in the equilibrium solution.

Table 3. Amount of K^+ sorbed by soil with variable charge and permanent charge

Soil treatment type	Amount of K+ sorbed (μg/g)		Desorbratio of K+ sorbed(%)	
	160μg/ml	400μg/ml	160μg/ml	400μg/ml
1 RNPK	846	1332	74.7	75.6
RNPKS	778	1265	78.1	74.6
GNPK	1726	3032	44.2	55.3
2 GNPKS	1583	2776	49.2	59.1

RNPKS: N=150(180) kg/ha, P_2O_5=90(90) kg/ha, K_2O=120(120) kg/ha, straw=2625(2625) kg/ha, applied for early (late) rice

GNKPS: N=Urea 255-300 kg/ha, P=superphosphate 180 kg/ha, K=KCl 75-150 kg/ha, straw=rice straw 4500-5250 kg/ha + wheat straw 3750-4500 kg/ha

- Data in table 3 indicated that When K^+ concentration in equilibrium solution was 160 μ g/ml and 400 μ g/ml,

1) the amount of K^+ sorbed by variable charge soil for the treatment RNPKS (being 778 and 1265 μ g/g) was lower than that in the treatment RNPK (being 846 and 1332 μ g/g), respectively.

2) The amount of K^+ sorbed by permanent charge soil for the treatment GNPKS (being 1583 and 2275 μ g/g) was lower than that in the treatment GNPK (being 1726 and 3032 μ g/g), separately.

Fig. 2. presented:

1) When K^+ adsorption reaction proceeded in the initial 30 minutes for variable charge soil and 100 min. for permanent charge soil, the accumulate adsorption amount of K^+ were no remarkable difference between the treatment RNPKS and RNPK or GNPKS and GNPK.

2) When the adsorption reaction proceed to reach equilibrium the accumulate adsorption amount of K^+ in the treatment of RNPKS and GNPKS being 470 μ g/g and 1586 μ g/g was lower than that in the treatment of RNPK and GNPK being 621 μ g/g and 1904 μ g/g, respectively.

Fig. 2. presented:

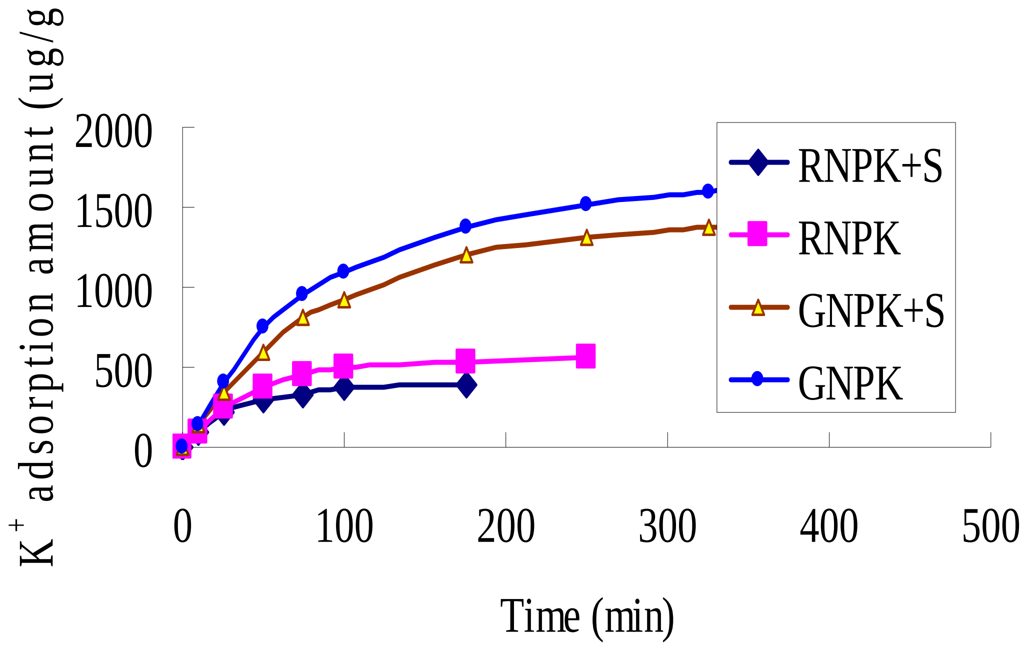

Fig.2. The change of adsorption amount of K^+ in soils tested with time goes on

Fig. 3. indicated that:

1) When the adsorption reaction proceed within the initial 100 min, the adsorb rate of K^+ in the treatment of RNPKS was remarkable lower than that of RNPK and then the difference between them was not clear.

2) When the adsorption reaction proceed within the initial 30 min.,the adsorb rate of K^+ in the treatment of GNPKS was slightly higher than that of GNPK, but it was evidently lower than that of GNPK, during the period of 30-230 min., and then the difference between them was not obvious.

Fig. 3. indicated that:

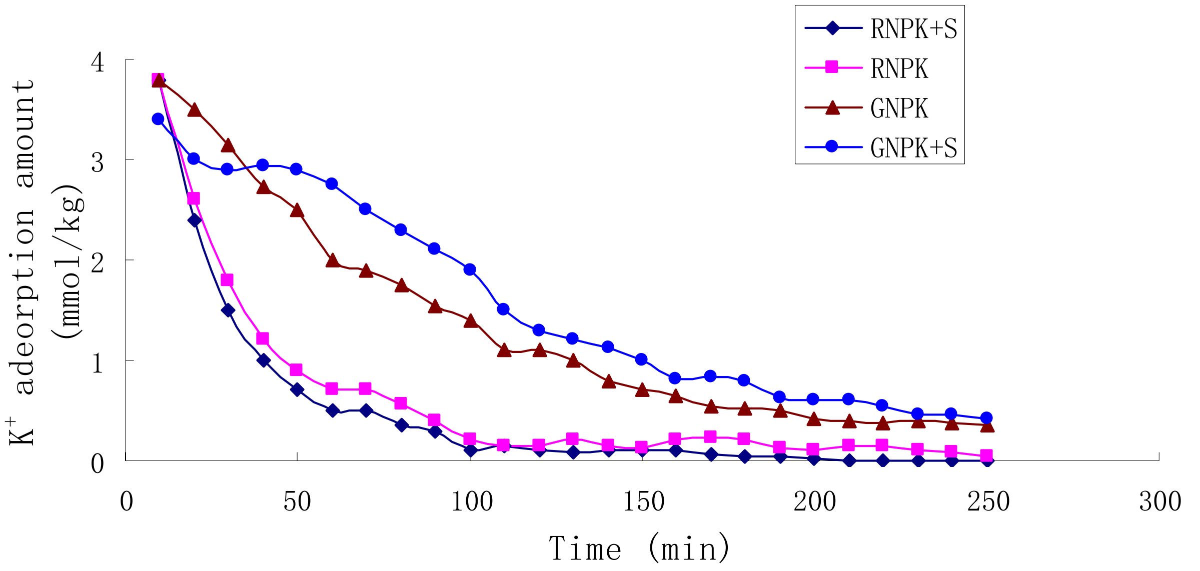

Fig. 3. The chang of adsorption amount of siol K$^+$ in per unit time with time goes on.

Fig. 4. and data in table 3. made known that:

1) When K^+ concentration in the equilibrium solution was 160 μ g/ml, the desorption amount and rate of K^+ sorbed on soil for the treatment RNPKS (78.1 μ g/g, 104.6%) and GNPKS (49.2 μ g/g, 111.3%) was higher than that of the treatment RNPK (74.7 μ g/g, 100%) and GNPK (55.3 μ g/g, 106.9%), respectively.

2) When K^+ concentration in the equilibrium solution was 400 μ g/ml, the desorption amount and rate of K^+ adsorbed on soils for the treatment RNPKS did not have obvious difference with the treatment RNPK, but for the treatment GNPKS still higher than that of the treatment GNPK.

Fig. 4.

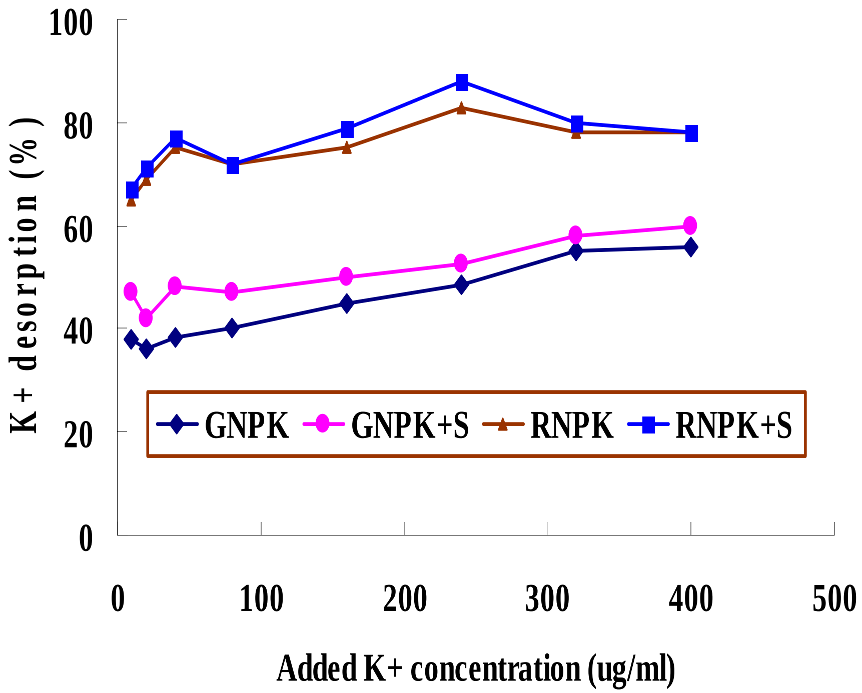

Fig.4. The desorption rate curves of K+ sorbed by soils tested.

Sum up the results mentioned above, we can see that:

1) As compared with the treatment of only application of NPK fertilizers, the treatment of returning straw to the field cooperated with application of N, P, K fertilizers could even more raise the amount of soil available K through reducing the amount of K^+ sorbed on soil and increasing its desorption amount.

2) The increase range for soil with permanent charge was higher than that of soil with variable charge.

4.2 Analysis and discussion

- Why the treatment of returning straw to the field could improve the adsorption-desorption characters of K^+ and raise the content of available K in soil, the main reasons will be analysised and discussed as follows.

- 1). As an example, of the K^+ removed by rice harvest, about 70% to 80% is present in the straw, returning straw to the field most of the K^+ taken up by the crop will return to soil which may increase the content of available K in soil.

- 2). K^+ sorbed by soil essentially is an electro-adsorption. Organic matter is through the surface negative charges mainly coming from the dissociation of proton of –COOH and –OH distributed on the organic constituents to adsorb K^+. The surface negative charges of soil organic matter are influenced by the properties, structure of their function groups, particularly by the pH of soil solution. The higher the soil pH, the higher the dissociation degree of the proton and the organic matter having more negative charges will be. Therefore, returning straw to the field would generally increase the source of soil negative charge and cover soil solid phase, the final results was either increase or reduce the amount of negative charge of soil particle surface which would depend on the influence of many factors.

- 3). It is fully proved that there were three kinds of function groups with various proton dissociation constants of organic matter in soil and dissociation constant of the first, second, and third kind was about 4-5, 7-8, and >10, respectively. The pH value of testing soil with variable charge being about 5, the organic matter carried only a few negative charge resulted from the first kind function group with partially dissociate proton. But the pH value of testing soil with permanent charge being 6.8-8.0, the organic matter carried more and more negative charges resulted from both the first and the second kinds function groups with partially dissociate proton.

- 4). The effect of returning straw to the field on the adsorption-desorption characters and the availability of K^+ in soil varied with various kinds soils. The essential reason was the difference of pH value in various kind soils and the considerable effect of different pH on the proton dissociation of function group in soil organic matter.

- 5). The influence of returning straw to the field on the adsorption-desorption character and availability of K^+ in variable charge soil was much weaker than that in permanent charge soil. The main reason was the difference of pH in two kind soils, which results in different dissociation degree of proton in function group of soil organic matter.

Thank you !