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Heating mixed solutions containing manganese sulfate, ammonium peroxodisulfate and ammonium sulfate at a molar ratio of 1:1:5 at 150°C gave NH_4–cryptomelane. The higher the starting manganese concentration, the higher the purity of the products. At a concentration of 0.5 mol/L any products other than NH_4–cryptomelane was detected. Column washing with 6 mol/L nitric acid was found to be suitable for exchanging NH_4^+ with H^+. The H–exchanged cryptomelanes were highly selective for K and the K adsorption capacity increased as the volume of nitric acid used for washing increased. The maximum adsorption capacity achieved in this study was about 800 mmol/kg.

Key words: cryptomelane, exchangeable potassium, non–exchangeable potassium, soilgao

INTRODUCTION

Potassium (K) is one of the three major essential elements (N, P and K) that have to be supplied as fertilizers in intensive agriculture. Unlike N and P, the average K content of soils is fairly high. According to the compiled data about the elemental composition of soils (Sparks, 1995), the average N and P content of soils are 2000 mg/kg and 800 mg/kg, respectively, whereas the K content is 14000 mg/kg. Nevertheless, most agricultural soils need annual high inputs of K fertilizers because most of the indigenous K in soils is not phytoavailable. The most part of indigenous K in soils reside in feldspars and mica occupying essential part of the mineral skeleton. They will be released via congruent and incongruent dissolution of the minerals but the rate of mineral weathering is not fast enough to meet the K requirement of crops.

The assessing phytoavailable K is, therefore, important in soil testing. Traditionally, most popular method for testing phytoavailable K is the extraction by neutral ammonium acetate solution either by column leaching (Schollenberger and Simon, 1945) or repeated batch extraction (Motomura *et al.*, 1992). The chemical forms of K extracted by these methods are water soluble K salts and K ions retained in interlayer spaces of expandable layer silicate minerals; typically smectite and vermiculite. Of these forms, the latter predominates and the fraction of K extracted by ammonium acetate methods is called exchangeable K. The exchangeable K is a good measure of phytoavailable K in many soils but there are many cases where this does not apply. Recently, for example, Fukuoka Agricultural Experimental Station had raised rice and wheat for five years in a row without any

K fertilizer and recorded normal yields (unpublished data). According to their soil testing the amount of exchangeable K was initially $0.61\,cmol_c/kg$ and it increased to $1.03\,cmol_c/kg$ at the end of the trial. This means that the conventional ammonium extraction method is of no use in the assessment of phytoavailable K in the soil. Many similar cases have been reported and some researchers are attempting at finding alternative method to better assess the phytoavailable K (Moritsuka, 2009).

The K supply without reduction of exchangeable K occurs via a slow release of so called non–exchangeable K that is probably reside at the periphery of micaceous minerals. When the K concentration in the soil solution decreases to extremely low levels, non–exchangeable K would undergo cation exchange reactions with other cations of relatively high concentrations (Scott and Smith, 1966). Thus, it is, in principle, difficult to discriminate exchangeable K from non–exchangeable K (Scott and Smith, 1966). This implies that the amount of K adsorbed by K–selective adsorbent that is brought to contact with a soil would be a good measure of K–supplying power of the soil. This idea was realized for phosphorus (P) and some heavy metals (Koster *et al.*, 2005). The adsorbents used for phosphorus were ferrihydrite (Menon *et al.*, 1997), zirconium hydroxide (Ding *et al.*, 2010) and Chelex resin was used for heavy metals (Davison and Zhang, 1994; Koster *et al.*, 2005). For K, cation exchange resin having sulfonate group was used (Martin and Sparks, 1985) but the assessment results were not satisfactory because of the lack in K–selectivity. Commercial cation exchange resins prefer multivalent cations including Ca^{2+} and Mg^{2+} rather than K+ (Helfferlich, 1962).

Recently the authors found that H–exchanged manganese cryptomelane, served as a K–selective adsorbent suitable for assessing the mobility of soil K (to be published). Cryptomelane is a manganese oxide having tunnel structure in which K ions are incorporated. The

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replacement of structural K^+ with H^+ by washing with acid makes a highly K–selective cation exchanger (Tanaka and Tsuji, 1994). However, the complete H–exchange is difficult and the presence of residual indigenous K causes some difficulty in soil K analyses. For soil analyses, NH_4–cryptomelane that contains NH_4 ions instead of K ions is more suitable. The synthetic method for NH_4–cryptomelane available in the literature (Li et al., 2007) but the optimum method for the preparation of the synthetic method and subsequent treatment method for H–saturation was not given. The objective of the present study was to find out the optimum and convenient method to prepare H–exchanged cryptomelane for soil K analysis.

MATERIALS AND METHODS

Synthesis of NH_4–cryptomelane and characterization

The synthetic scheme reported by Li et al. (2007) was used to prepare NH_4–cryptomelane in this study. The basic procedure was to autoclave a mixed ammonium peroxodisultate–manganese(II) sulfate–ammonium sulfate solution. Li et al. (2007) implied that a molar ratio of 1:1:5 was suitable but gave no information of the solution concentration. In this study the effect of the concentration of starting solution on the purity and crystallinity of the products was examined.

Analytical grade reagents of $(NH_4)_2S_2O_8$, $MnSO_4 \cdot 5H_2O$ and $(NH_4)_2SO_4$ were dissolved in distilled water at a molar ratio of 1:1:5 and at concentrations of 0.1, 0.25 and 0.5 with respective to Mn. Fifty mL portions of the prepared starting solutions were placed in Teflon–lined stainless autoclave and heated for 24 h in an electric oven kept at 150°C. After cooling to room temperature, the formed dark brown precipitates were repeatedly washed with distilled water by filtration using $0.45\,\mu m$ membrane filters. The collected products together with the filters were transferred to weighing bottles, dried at 50°C and weighed.

The dried products were characterized by X–ray diffraction (XRD), differential thermal analysis (DTA) and chemical analysis. In the XRD, a part of a product was packed in a glass holder with a depth of 0.5 mm and examined in a Rigaku RINT 200V diffractometer using Cu Kα radiation. Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were done with a Rigaku ThermoPlus Evo analyzer at a heating rate of 10°C/min. For chemical analysis, 0.1 g portion of a product was dissolved in 30 mL of 0.2 mol/L sodium oxalate acidified with H_2SO_4. The NH_4 concentration of the digest was determined by microdiffusion method (Conway and O'Malley, 1942) using 20 g/L boric acid solution containing mixed bromocresol blue–methyl red indicator as NH_3–absorbent and a mixed 150 g/L MgO suspension as alkalinizing agent. Since so called Conway unit for microdiffusion analysis was not available, a mall petri dish containing 1 mL of the borate absorbent and another small petri dish to which 1 mL of the digest and 3 mL of MgO suspension were placed at the opposite sides were placed in an air–

tight plastic bag. The bag was thermally sealed, gently rolled to mix the digest and MgO suspension, and allowed to stand for 24 h. The borate absorbed was backtitrated with 2.5 mmol/L H_2SO_4 to the original color.

H–exchange

Batch– and column–washing were carried out using a cryptomelane synthesized from 0.5 mol/L starting solution. In batch washing, 0.4 g portions of cryptomelane were placed in a glass centrifuge tubes and 30 mL portions of 6 mol/L nitric acid were added, mixed by vigorous shaking and centrifuged. After prescribed number of acid–washing, they were repeatedly washed with distilled water until the pH of the supernatant became neutral and dried at 50°C.

In column washing, portions of suspension containing 0.45 g of cryptomelane was put in four glass columns of 19 mm in diameter and the excess water was drained. The height of the cryptomelane bed was about 4 cm. The columns were connected to 6 mol/L nitric acid reservoir and eluted at a flow rate of about 100 mL/h. After elution of 250, 500, 1000, and 1500 mL, the nitric acid was replaced by distilled water and washed until the eluent became neutral. The washed samples were dried at 50°C.

In addition to washing with nitric acid, dried NH_4–cryptomelane was heated for 1 h at 350°C to turn it into H–cryptomelane (Liu et al., 2003). The expected reaction is

$$NH_4X(s) = HX(s) + NH_3(g) \tag{1}$$
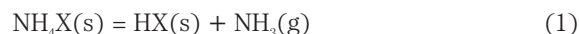
where X stands for negatively charged site in the cryptomelane.

The prepared H–cryptomelanes were characterized by K adsorption experiments, in which 0.1 g of the prepared H–cryptomelane was equilibrated with 10 mL of 2 to 10 mmol/L potassium chloride solutions and the potassium adsorption was calculated from the difference in potassium concentration. The potassium concentration was determined by atomic absorption spectroscopy (Hitachi Z–2300).

RESULTS AND DISCUSSION

Dissolution of $(NH_4)_2S_2O_8$, $MnSO_4 \cdot 5H_2O$ and $(NH_4)_2SO_4$ in distilled water resulted in clear solution. It gradually turned pale brown on standing at room temperature particularly at a Mn concentration of 0.5 mol/L. After heating, dark product precipitated at the bottom of the reaction vessel leaving colorless clear solution. This indicates that the oxidation reaction proceeded and Mn(II) in the starting solutions was quantitatively oxidized to form manganese oxides during heating in the autoclave at 150°C. The reaction was

$$Mn^{2+} + S_2O_8^{2-} + 2H_2O = MnO_2 + 2SO_4^{2-} + 4H^+ \tag{2}$$

where the peroxodisulfate ion worked as an oxidizing agent and Mn^{2+} was oxidized mostly to Mn^{4+} leaving some Mn^{3+}. The trivalent Mn gives the lattice net negative

charges and they are neutralized by retention of NH_4^+. The net weights of the desalted and dried products were, 0.452 g and 1.122 g and 2.311 g for 50 mL starting solutions of 0.1 mol/L, 0.25 mol/L and 0.5 mol/L $MnSO_4$. The expected yields of the products on an assumption that the reaction products were pure MnO_2 are 0.435 g for 0.1 mol/L, 1.087 g for 0.25 mol/L and 1.173 g for 0.5 mol/L. The actual yields were close to the theoretical ones but significantly larger, suggesting that the progress of the oxidation reaction was almost complete and the products retained substantial amounts of NH_4^+ and water.

Fig. 1 shows the XRD patterns of the products, on which numbers indicated at the left end of the patterns are the Mn concentrations in the starting solution. All the diffraction except for one at 22.3° were assigned to the peaks of cryptomelane (α–MnO_2). The peak at 22.3° is assigned to γ–MnO_2 and its intensity decreased as the solution concentration increased. At 0.5 mol/L, it was not
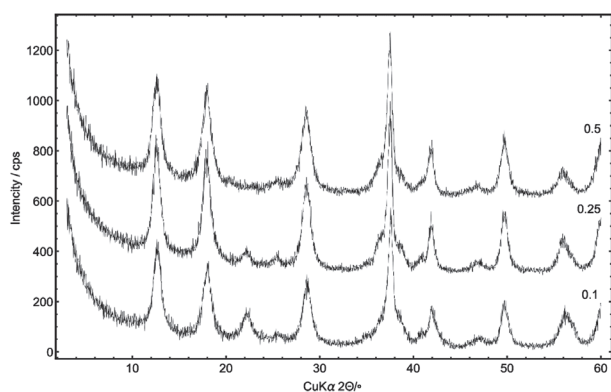

Fig. 1. X–ray diffraction patterns of the products from solutions with different manganese concentrations. The numbers at the left margin of the graph indicate the manganese concentrations of the starting solutions.

discernable. The result that purer cryptomelane phase is obtained at higher concentrations is fortunate for the preparation of adsorbent.

The XRD peaks (Fig. 1) were significantly broader than those of dry–synthesized cryptomelane from manganese carbonate and potassium–tert–butoxide (Tanaka and Tsuji, 1994). This may be due to the nm–sized of the present products (Li *et al.*, 2007).

DTA–TG curves of the two products are shown in Fig. 2. The product from a starting solution of 0.1 mol/L Mn (left) showed two clear endothermic peaks at 40°C and at 550°C and 4 steps of weight loss in temperature ranges from 25 to 100°C, 150 to 300°C, 450 to 600°C and 700 to 800°C and the first and third weight loss accompanied corresponding clear endothermic peak. Feng *et al.* (1999) and Li *et al.* (2007) reported similar results on synthetic NH_4–cryptomelanes, although the second and fourth weight losses were not well resolved in the preceding studies. The first and second weight losses are probably due to desorption of water adsorbed on external surfaces and decomposition of ammonium ions (Eq. (1)). The third and the largest weight loss at 450 to 600°C can be assigned to the phase transition from cryptomelane to Mn_2O_3 (Feng *et al.*, 1999; Li *et al.*, 2007). The product from 0.5 mol/L solution gave similar DTA–TG results but the third weight loss was significantly larger.

In the product from 0.5 mol/L solution, the loss of weight by water desorption was 0.35 mg, that by ammonium decomposition was 0.45 mg, and the loss due to the phase transition was 0.8 mg (Fig. 2, right). These values and the initial weight of the sample (10.0 mg) give the ammonium content of 2738 mmol/kg, which is two times larger than the experimental value (Table 1). This large misfit is probably because the second weight loss was due not only to the decomposition of NH_4^+ but also to desorption of water retained in the tunnels. The weight of the sample after the decomposition of NH_4^+ was 9.2 mg
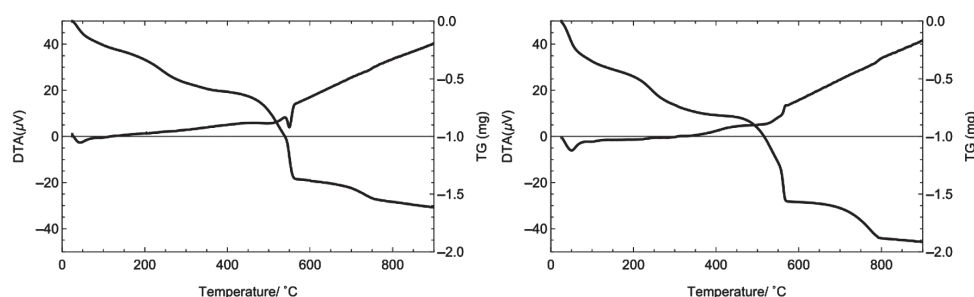

Fig. 2. DTA and TG curves of the products from 0.1 mol/L solution (left) and 0.5 mol/L solution (right).

Table 1. Chemical composition of synthetic manganese oxides

Mn concentration/ mol L^{-1}	NH_4 content/ mmol kg^{-1}	Chemical formula
0.1	1109±15	$NH_{4\,0.09}(Mn(III)_{0.09}Mn(IV)_{0.91})O_2$
0.25	1211±20	$NH_{4\,0.10}(Mn(III)_{0.10}Mn(IV)_{0.90})O_2$
0.5	1267 ± 14	$NH_{4\,0.11}(Mn(III)_{0.11}Mn(IV)_{0.89})O_2$

(= 10.0 – 0.35 – 0.45). The expected loss of weight due to the MnO_2 to Mn_2O_3 phase transformation is 0.85 mg and this is close to the measured weight loss of 0.8 mg in the 450 to 600°C range.

The ammonium content of the products (Table 1) were 1109 mmol/kg, 1201 mmol/kg and 1267 mmol/kg for starting Mn concentration of 0.1, 0.25 and 0.5 mol/L, respectively and it increased as the Mn concentration increased. This is probably due to the formation of γ–MnO_2 in solutions having lower Mn concentrations (Fig. 1). Using these values the chemical formulae were calculated and listed also in Table 1. The calculated proportions of the trivalent Mn ranged from 0.09 to 0.11 and these values are in between the values reported by Li *et al.* (2007) and those by Galindo *et al.* (2010). Li *et al.* (2007) reported that some oxygen vacancy may occurred form the presence of mixed valence of Mn ions, suggesting that the formulae listed in Table 1 should be taken as approximate ones.

The K adsorption capacity of H–cryptomelanes differed depending on the mode and the concentration of nitric acid used. In general, the higher the concentration of nitric acid the higher the K adsorption capacity. In batch washing 4 repeated washing with 6 mol/L nitric acid achieved the K adsorption capacity of 500 mmol/kg. However, the washing by centrifugation using concentrated nitric acid and fragile glass centrifuge tubes was considered to be inadequate as a routine method for H–cryptomelane preparation in view of safety and efficiency.

The K adsorption behavior of H–cryptomelanes prepared by column washing with 6 mol/L nitric acid is graphically shown in Fig. 2, where the K adsorption is plotted against equilibrium K concentration (adsorption isotherm). The adsorption isotherm for heat–treated cryptomelane is also shown in the same figure. The shape of the adsorption isotherms were almost perpendicular to abscissa, indicating that the prepared H–cryptomelanes were selective for K. The curves declined at fairly low K concentrations to plateau. The adsorption capacity estimated from the position of the plateau of the curves were about 380, 450, 760 and 870 mmol/kg for the samples washed with 250, 500, 1000, and 1500 mL of nitric acid, respectively. The estimated adsorption capacity is plotted against the volume of the nitric acid in Fig. 4. This graph shows that the adsorption capacity increased as the volume of the washing acid solution increased.

Theoretically, the maximum K adsorption capacity is equal to the amount of NH_4^+ retained in the starting cryptomelane, i. e., about 1270 mmol/kg. It is not clear from the trend in Fig. 4 whether the complete replacement of NH_4^+ with H^+ is possible or not but it will probably possible to attain adsorption capacity around 1000 mg/kg. In the present washing trials, the flow rate of nitric acid was too fast and it is not realistic to prepare large amounts of H–cryptomelane having high adsorption capacity with this manner. Further study to find out suitable flow rate and practical goal of adsorption capacity is still needed.

Liu *et al.* (2003) reported that they prepared H–cryptomelane by heating NH_4–cryptomelane at 350°C.

The NH_4–cryptomelane synthesized in the present study was heated in a way reported by Liu *et al.* (2003). The XRD patterns before and after heat treatment (Fig. 5) show that heating kept all the diffraction peaks and greatly sharpened them, suggesting that the crystallinity was improved. It was noted that major peaks shifted to lower angles and this may be due to the loss of NH_4^+ ions that support the skeleton.
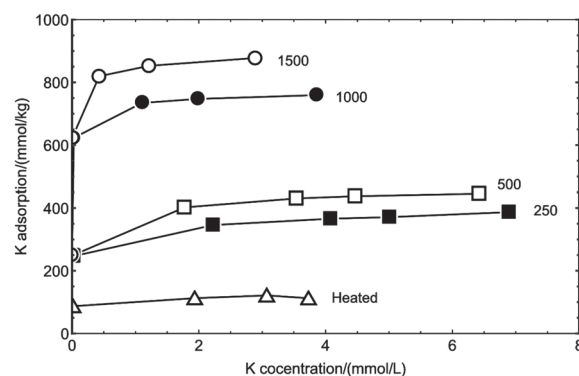

Fig. 3. Potassium adsorption isotherms of the H–exchanged cryptomelanes. The numbers indicate the volume of nitric acid (mL) used for washing.
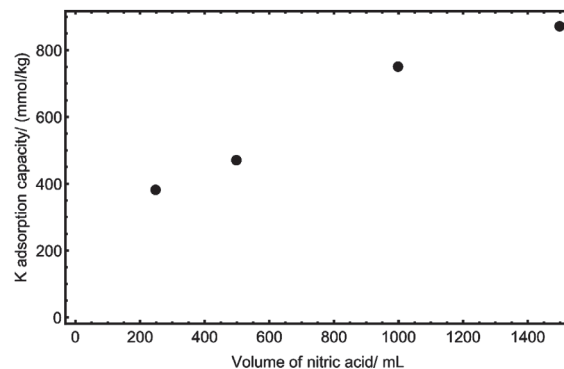

Fig. 4. The K–adsorption capacity plotted against the volume of nitric acid for washing.
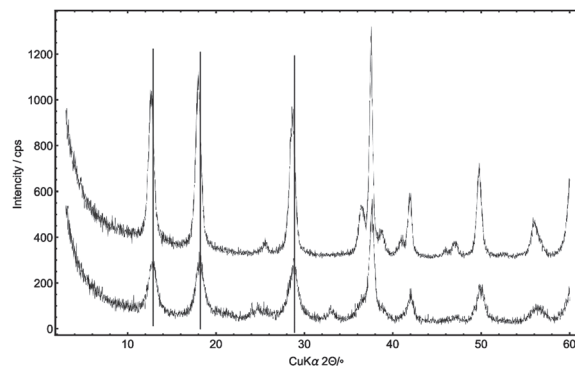

Fig. 5. X–ray diffraction patterns of a cryptomelane before heating (bottom) and after heating at 350°C (top).

The K adsorption isotherm of heated sample (Fig. 3) shows that the maximum K adsorption was only about 140 mmol/kg. This great reduction in K adsorption capacity is probably due to the oxidation of structural Mn(Ⅲ) to Mn(Ⅳ). Heating at 350°C is very convenient method for preparation of H–cryptomelane but the heating in the air gives no satisfactory results. Heating in an inert gas may result in larger adsorption capacity.

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