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Synthesis and Physicochemical Characterization of Pure Diammonium Phosphate from Industrial Fertilizer

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ABSTRACT: Diammonium phosphate (DAP) is produced from industrial phosphoric acid that contains large amounts of anionic and cationic impurities (Co, Cu, Fe, Mn, Mo, Ni, Zn, F, As, Al, Hg, Pb and Cd). Consequently all those impurities will be found in DAP. However, the industrial DAP obtained can be used as fertilizers, but cannot be used for some industrial application like pharmaceutics and cosmetics. After purification, the price of DAP is three times more expensive than the same product before purification. The procedure for purification of industrial DAP is a recrystallization, by using several mixtures of solvents. The physicochemical characterization of this fertilizer upstream and downstream from the purification, through spectroscopic analyses and chemical analyses, shows that recrystallization eliminates impurities. Purified DAP was obtained, the physicochemical properties of which are comparable to those of the pure commercial DAP (Fisher).

1. INTRODUCTION

Diammonium phosphate (DAP) is an important commercial fertilizer. The important water-soluble P fertilizers include monoammonium phosphate (MAP) and diammonium phosphate (DAP).[1] The fertilizer is produced industrially in large quantities via the reaction between gaseous ammonia and green phosphoric acid. The reaction is exothermic; the equation for the neutralization reaction between ammonia and phosphoric acid is as follows:[2]

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2HPO_4$$

When the molar ratio (MR) of ammonia to phosphoric acid is 2, DAP is formed.[2] The phosphoric acid used in producing DAP can be crude unpurified acid obtained by dissolving phosphate rock with sulfuric acid. In this case, crude DAP results, which may be adequate for some applications. However phosphate rock may contain heavy metals and these can be transferred to the fertilizer, and further to crops.

Two options are available to produce purified DAP: (1) use purified phosphoric acid; (2) purify the DAP. For producing industrial purified diammonium phosphate from wet process phosphoric acid, it is necessary to purify the phosphoric acid in advance according to a process of extracting phosphoric acid from wet process phosphoric acid according to a solvent process, followed by reacting ammonia with the resulting extract to obtain diammonium phosphate containing a small amount of impurities. However, this extraction process cannot be regarded as an industrially advantageous process owing to its complicated steps.[3]

Our work began with the purification of monoammonium phosphate (MAP) from industrial fertilizer, and the results are very encouraging.[4] This prompted us to pursue this study on another product of the same family, DAP.

In the present work, we are interested in eliminating impurities from industrial DAP. We present here the physicochemical characterization of DAP fertilizer upstream and downstream of the purification process, with an aim to determine the performance

Table 1. Chemical Compositions of the DAP Upstream and Downstream from the Recrystallization

samples	P_2O_5 (wt) %	N (wt)%	H_2O (wt) %	MR (N/P)	pH
plant DAP	46.05	17.65	1.50	1.94	7.6
plant DAP recrystallized	49	18	1.68	1.86	7.9

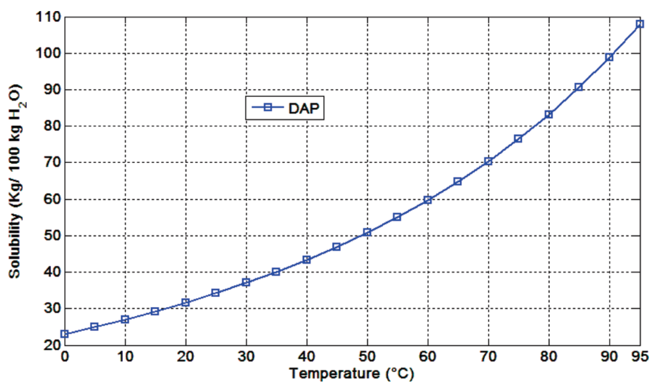

Figure 1. Curve solubility of recrystallized DAP.

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Table 2. Determination the Impurity Present in the DAP Upstream and Downstream from the Recrystallization[a]

sample (ppm)	Fe	Al	Mg	Ag	As	Co	Pb	Hg	Si	Sn	Ti	Cr	Zn	Cd	Cu	Ni	Mn	V
plant DAP	6769	4273	4907	6	26	5419	22	3	150	382	93	525	1203	34	59	25	65	1341
plant DAP recrystallized (water-alcohol)	24	37	14	-	3	3	7	-	70	-	2	27	41	3	4	17	1	47
commercial DAP (Fisher)	15	22	9	-	3	2	7	-	38	-	-	25	11	3	2	17	-	9

[a] Dash (-) = trace.

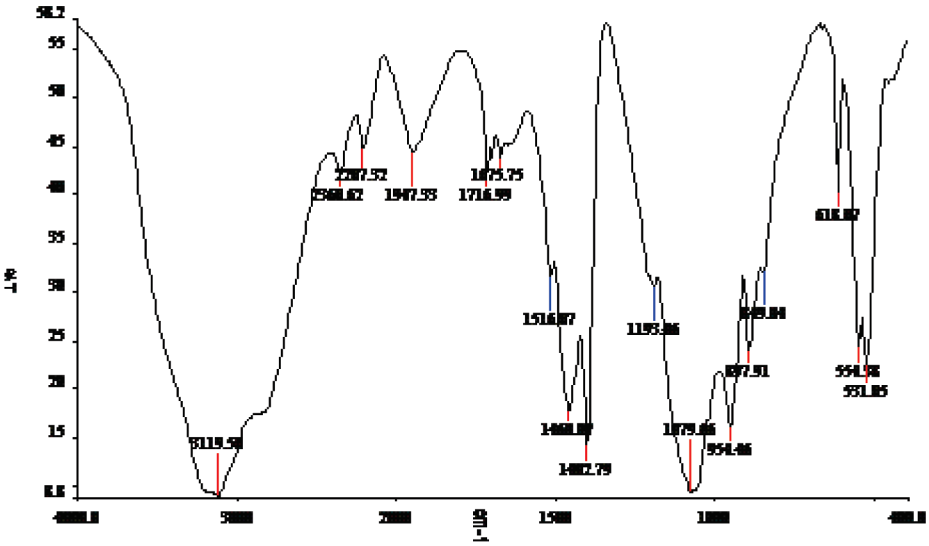


Figure 2. The analysis by means of IR of the industrial DAP upstream from the recrystallization.

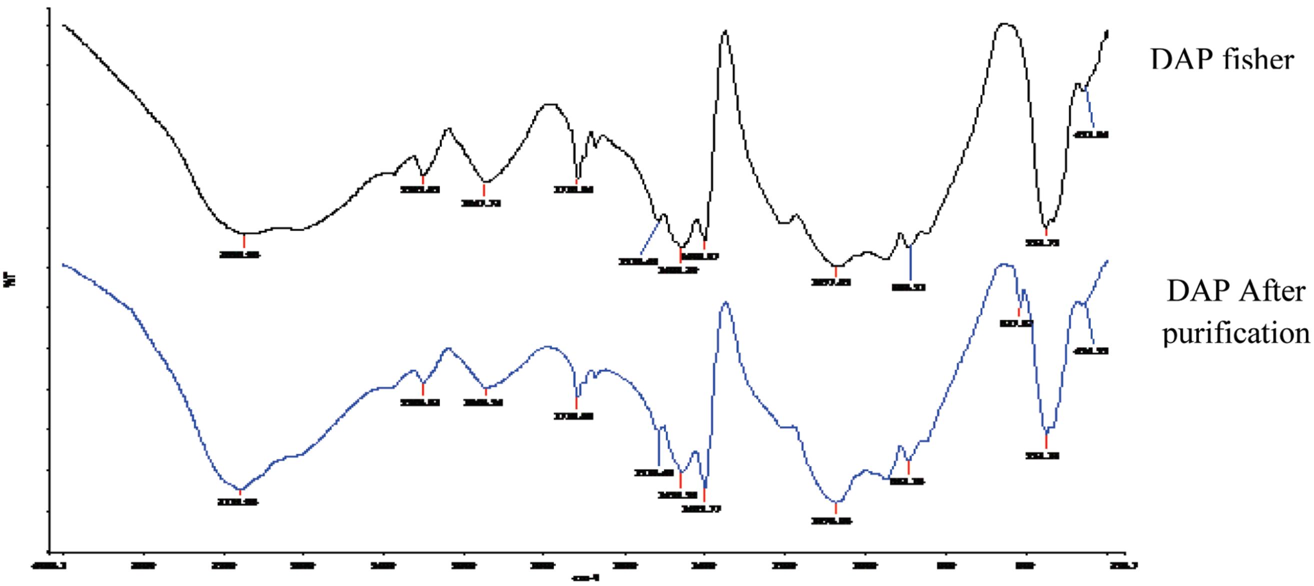
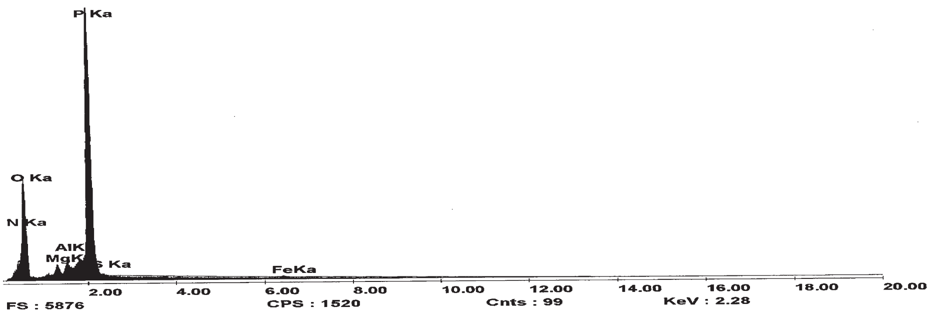


Figure 3. The analysis by means of IR of the industrial DAP downstream from the recrystallization and pure commercial DAP (Fisher).

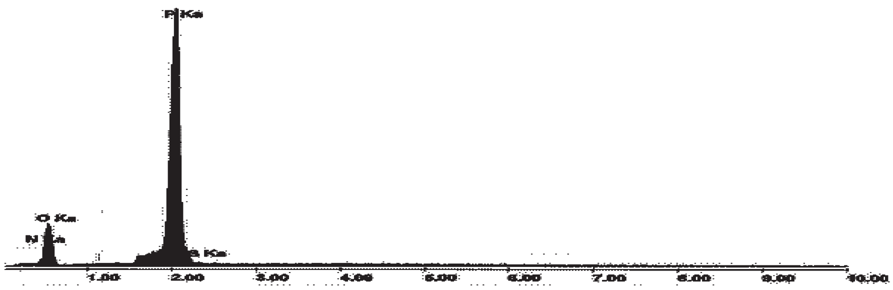
of recrystallization. We also compare the recrystallized DAP to the commercial DAP (Fisher).

2. EXPERIMENTAL SECTION

2.1. Recrystallization. Crystallization experiments of DAP (fertilizer synthesized in industry from Tunisia) were carried between 273 and 400 K and at 400 rpm stirring rate. The suspension was dissolved in mixed solvent (70% water—30% alcohol). After that we add a quantity of charcoal in the solution. The suspension was filtered, and the solution was cooled to 273 K, whereupon crystals appeared. We recrystallized the DAP using a mixture of solvent, water, and alcohol. Impurities were analyzed by inductively coupled plasma-optical emission spectroscopy (ICPOES).



a. upstream from the recrystallization



b. downstream from the recrystallization

Figure 4. The analysis by MEB of the industrial DAP upstream and downstream from the recrystallization.

Table 3. The Wavelength of the Vibration Mode of DAP Upstream (ur) and Downstream (dr) from the Recrystallization and Pure Commercial DAP (Fisher)

bands	band limit of absorption (cm^{-1})[8,9]	DAP (ur)	DAP (dr)	pure commercial DAP (Fisher)
PO_4^{3-}	υ_1: 1000−800	954	886	893
	υ_2: 500−300	531	454	451
	υ_3: 1200−1000	1097	1076	1077
	υ_4: 650−500	618	553	553
NH_3	∂_a: 1600−1575	1516	1516	1516
	∂_s: 1500−1300	1400	1403	1402
NH_4^+	υ_{NH}: 3300−3030	3119	3119	3099
H_2O	υ_{OH}: 3600−3100	3119	3119	3099

2.2. Analytical and Testing Methods. P_2O_5 content in the solution is determined gravimetrically. The molar rapport of ammonia to phosphoric acid (MR) was obtained by titration with standard 0.5 M NaOH and 0.5 M HCl solutions. The amount of HCl and NaOH added was used to calculate the MR that is equal to 2 (volume of NaOH/volume of HCl), according to the method described in ref 5. A pH Meter was employed to measure the pH values of slurries. N content in the solutions was determined by the Kejdahl method. Melting points were determined with a METTLER FP62 that uses a capillary tube. The curve solubility was determined following a standard procedure described by Mullin.[6] IR spectra were determined by a FTIR system spectrum BX Perkin-Elmer spectrometer. The analysis by scanning electron microscope (SEM) is determined with a MEB Philips série XL 30. Data collection is realized by using KappaCCD Server Software (Nonius, 2004); program(s) used to solve structure are SHELXS97. The spectra of X-ray powder diffraction (XRPD) is determined by a Seifert 3000. T.T. spectrometer.

3. RESULTS AND DISCUSSION

The principal chemical compositions of the DAP upstream and downstream from the recrystallization are presented in Table 1. After purification, the % P_2O_5 and % N were increased while keeping the molar ratio (MR) range between 1.8 and 2.0. Also, after purification the percentage of H_2O and value of pH are slightly changed but in the various ranges stated. There is 25% of impurities by weight in the crude industrial DAP.

Diammonium phosphate granules contain various compounds (Ca, Mg)(NH_4)(Fe, Al)(PO_4)(F, OH)H_2O that are insoluble in water and can comprise up to 10% of the total P content of fertilizers.[7] The DAP contains toxic elements such as (Cd, Zn, Cu, and Ni) which are toxic for plants and have the potential for adverse effects on human health due to the transfer of metals from soils to food corps. Thus, it is important to eliminate or reduce these toxic elements in DAP. The analysis of the DAP after purification is given in Table 2 and shows that the quantity of impurity decreases. The results are comparable to those of the commercial DAP (Fisher).

After recrystallization, the melting point was found to be 194 °C, close to the one of laboratory grade DAP (196 °C).

The curve solubility of recrystallized DAP, that was determined following a standard procedure described by Mullin,[6] is shown in Figure1. The solubility of a solute is most conveniently stated as the parts by weight per part (or 100 parts) by weight of solvent.

The analysis by means of IR of the DAP before and after recrystallization is presented in Figures 2 and 3.

Table 4. Crystal Data Details and Structure Refinement of the Plant DAP Downstream from the Recrystallization and Commercially Pure DAP

	DAP recrystallized	pure commercial DAP (Fisher)
I. Crystal Data		
formula	$(NH_4)_2HPO_4$	$(NH_4)_2HPO_4$
formula weight (g/mol)	132.06	132.06
system	monoclinic	monoclinic
space group	*P*21/*c*	*P*21/*c*
a (Å)	10.781(2)	10.729(5)
b (Å)	6.771(2)	6.682(5)
c (Å)	8.047(2)	8.009(5)
□	109.72(2)	109.670(5)
V (Å^3)	448.1 (2)	540.7(6)
Z	4	4
ρ_{cal} (g cm^{-3})	1.600	1.622
F (000)	280	332
μ (Mo Kα) (mm^{-1})	0.427	0.433
crystal color	colorless	colorless
II. Intensity Measurements		
temperature (K)	293 (2)	293 (2)
wavelength Mo Kα (Å)	0.71073	0.71073
measurement area:		
h	$-13 < h < 13$	$-12 < h < 12$
k	$-1 < k < 8$	$-7 < k < 7$
l	$-10 < l < 7$	$-9 < l < 9$
III. Structure Determination		
unique reflections included with $I > 2\sigma(I)$	1124	765
refined parameters	100	101
unweighted agreement factor R_1[a]	0.0231	0.0262
weighted agreement factor Rw_2[a]	0.0660	0.0783

[a] *R* values are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $Rw_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w^{-1} = [\sigma^2(F_o^2) + (0.0442P)^2 + 2.4726P]$ and $P = (F_o^2 + 2F_c^2)/3$.

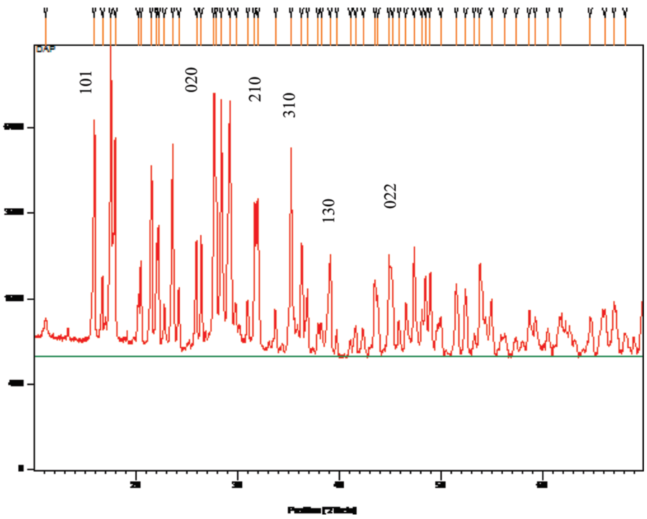


Figure 5. The analysis by XRPD of the industrial DAP.

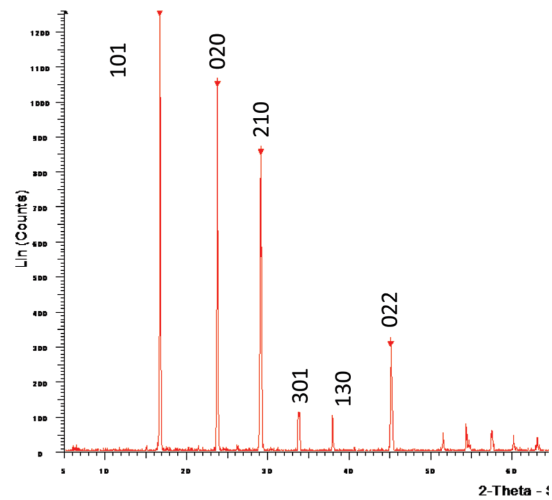


Figure 6. The analysis by XRPD of the industrial DAP downstream from the recystallization.

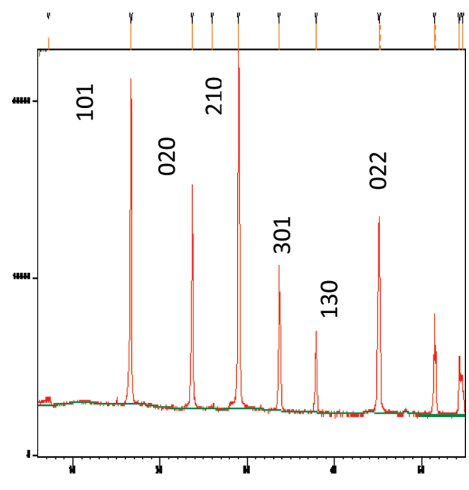


Figure 7. The analysis by XRPD of the pure commercial DAP (Fisher).

The characteristic wavelengths of the vibration modes of DAP are illustrated in Table 3, which shows the presence of the four modes of vibrations ascribed to PO_4^{3-} observed at about 444, 539, 917, and 1110 cm^{-1}, the vibrations of ammonia observed about 1400 cm^{-1}, and a wide band attributed to H_2O and NH_4^+ stretching modes observed around 3137 cm^{-1}.

In addition, the analysis by sweeping electron microscope (MEB) of the industrial DAP after recrystallization, showed that the elements of aluminum, magnesium, and copper are eliminated, and the quantity of sulfur was decreased (Figure 4).

The crystal structure of the recrystallized diammonium phosphate $(NH_4)_2HPO_4$ has been determined by X-ray single crystal analysis at room temperature. The space group is *P*21/*c*[10] with lattice parameter $a = 10.781(2)$ Å, $b = 6.771(2)$ Å, $c = 8.047(2)$ Å, and $Z = 4$. The refinement converged to $R_1 = 0.0231$ and $R_{W2} = 0.0660$. The analysis by X-ray diffraction showed that the purification of the DAP did not change the crystalline system (monoclinic). Crystal data details and structure refinement are given in Table 4 and show that the crystallographic parameters of

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recrystallized DAP are close to the pure DAP (Fisher), which justifies the performance of the recrystallization.

In addition, the analysis by X-ray powder of industrial DAP downstream of the purification (Figure 6) shows an elimination of the impurities that were found upstream of the purification (Figure 5), and we got a good crystalline product that resembles the pure commercial DAP (Fisher) (Figure 7).

4. CONCLUSION

The long-continued application of impure DAP can redistribute and elevate heavy metal concentrations in soils. The redistribution of heavy metals can adversely affect water resources and endanger the health of surrounding ecosystems and human populations. Thus, it is important to eliminate the different toxic elements present in the fertilizer in order to prevent transfer to plants and humans, in this case with the use of purified fertilizers in biological agriculture. On the other hand, you can also use the purified product in the pharmaceutics and cosmetic industries.

After purification, the % P_2O_5 and % N increased, while the molar ratio (MR) remained between 1.8 and 2.00 and the products obtained contained 1.5−2% H_2O and had a pH value of 7−8. The analysis by X-ray diffraction showed that the purification of the plant DAP did not change the crystalline system (monoclinic).

The physicochemical characterization of the industrial DAP downstream of the purification, through spectroscopic analyses and chemical analyses, showed that we obtained purified DAP whose physicochemical properties are comparable with those of the pure commercial DAP (Fisher).

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■ REFERENCES

(1) Duraisamy, V. P. Role of inorganic and organic soil amendments. *Aust. J. Soil Res.* **2005**.

(2) Campbell, G. R.; Leong, Y. K.; Berndt, C. C.; Liow, J. L. Ammonium phosphate slurry rheology and particle properties The influence of Fe(III) and Al(III) impurities, solid concentration, and degree of neutralization. *Ind. Eng. Chem. Res.* **2006**, *61*, 5856–5866.

(3) Akiyama, A. Studies on chemical fertilizers. *K.K. Nissin Syuppan* **1976**.

(4) Gargouri, M.; Chtara, C.; Charock, P.; Nzihou, A.; Elfeki, H. Synthesis and physicochemical characterization of pure monoammonium phosphate (MAP) from industrial fertilizer. *J. Chem. Chem. Eng.* **2010**, *49*, .

(5) Shengwei, Tang; Hui, Guo; Jiankang, ying; Bin., Liang Physicolchemical propreties of acidic ammonium phosphate slurries. *Ind. Eng. Chem. Res.* **2004**, *43*, 3199.

(6) Mullin, J. *Crystallization*; Butterworth-Heinemann : Oxford, GB, 2001.

(7) Gilkes, R. J.; Mangano, P. Poorly soluble iron-aluminium phosphates in ammonium phosphate fertilizers: Their nature and availability to plants. *Aust. J. Soil Res.* **1983**, *21*, 183–194.

(8) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1984.

(9) Parker, F. S. *Application of IR Spectroscopy in Biochemistry, Biology and Medicine*; Hilger, A., Ed.; Plenum Press: New York, 1971.

(10) Khan, A. A.; Roux, J. P.; James, W. J. The crystal structure of diammonium phosphate, $(NH_4)_2HPO_4$. *Acta Crystallogr., Sect. B* **1972**, *28*, 2065–2069.