



SYNTHESIS OF DICALCIUM PHOSPHATE USED AS FEED ADDITIVE FOR ANIMALS FROM PHOSPHATE ROCK AS POTENTIAL COST-EFFECTIVE RAW MATERIAL

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ABSTRACT

Dicalcium phosphate (DCP) an animal feed additive was synthesized from phosphate rock under optimum condition of pH, temperature of reaction mixture, time of reaction and acid concentration. Concentrated slurry of 200 mesh sieve calcium hydroxide was used to remove impurities. Solution was filtered and pH of filtrate was again adjusted to precipitate dicalcium phosphate. Dicalcium phosphate was filtered, washed, dried and grinded. The best values in terms of quality and quantity of dicalcium phosphate from locally phosphate rock were achieved at acid concentration of 10% w/w, reaction time of 1.5 hrs, at 30°C and pH values of 2.3-2.4 (during precipitation of impurities) and 5.5-5.6 (for the final synthesis of dicalcium phosphate). Pure dicalcium phosphate (98.20%) was prepared using above method. Purity of the dicalcium phosphate in terms of phosphorus content and total assay were determined using ICP-OES and British Pharmacopoeia, respectively. Impurities like fluorides were determined by ISE, and arsenic, barium, iron, aluminium, magnesium and lead by ICP-OES, while chlorides and sulphates were determined by UV-Vis Spectrophotometer. The amount of impurities found were fluorides (80.02 ppm), Iron (360.2 ppm), arsenic (3.41 ppm), lead (22.08 ppm), aluminium (5.04 ppm), chlorides (240.8 ppm), barium (5.04 ppm), magnesium (155.27 ppm) and sulphates (0.303 %).

Key words: Dicalcium phosphate, ICP-OES, ISE, UV-Vis Spectrophotometer.

INTRODUCTION

Major mineral components of the skeleton are calcium and phosphorus. The bones stores 80 percent of phosphorus and 90 percent of calcium of total body weight. The dietary inadequacies of calcium and phosphorus on short term basis gained from skeletal stores. The bones become weaken or even breakage occurred by long term deficiencies of calcium and phosphorus¹. Cattles need calcium for skeletal growth and milk production. Phosphorus is required for tissue development, bone, energy utilization; also in animal body has more

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known functions than any other mineral². Hypocalcaemia is of particular concern for dairy animals within a few days of parturition. 1-hydroxylation of 25-hydroxycholecalciferol are consequences of PTH formation due to prevention of hypocalcaemia by taking calcium in late pregnancy, which enhance absorption of dietary calcium and resorption of skeletal calcium³. Hypophosphatemia (phosphorus deficiency) may cause symptoms related to young cattle growth retardation, appetite and milk yield reduction and impaired fertility. Osteomalacia caused skeletal abnormalities, which may appear as stiffness, movement reluctance, shifting lameness, joints cracking sounds on walking; an arched back and, spontaneous fractures in severe cases⁴. Inorganic phosphate rock of both sedimentary origin and igneous has been used in the production of feed supplements as a source of phosphorus for farm and domestic animals during the last several decades⁵. At 25°C mixing of ortho-phosphoric acid with calcium hydroxide suspension in equimolar quantities has been investigated for precipitation of dicalcium phosphate dihydrate and brushite. Before mixing the concentration of ortho-phosphoric acid and calcium hydroxide ranged from 50 to 300 mmol/L. $\text{Ca}_5\text{OH}(\text{PO}_4)_3$, hydroxyapatite precipitated in first phase. The brushite precipitation process divided into five stages and is similar for all initial experimental conditions. The extension of each stage varies with the initial reagents' concentrations. Each stage was discussed individually as a function of reagents concentrations and pH. X-ray diffraction and scanning electron microscopy used for analysis of precipitates. The brushite solubility was determined in the pH range 4.5-8.0 at 25°C, 30°C and 35°C⁶. Wet acid digestion of the phosphate rock with sulphuric acid and hydrochloric acid is commonly used for dicalcium phosphate production both acids used also lead to the enhancement of several radionuclides within the final product^{7,8}. When phosphate rock is treated with hydrochloric acid even lower values of magnesium, iron and aluminium are eliminated during its coprecipitation with calcium fluoride⁹. A study indicated that the biological availability of dicalcium phosphate is 93-95 %¹⁰. The objective of present study was to synthesize the dicalcium phosphate (DCP), an animal feed additive approved by FDA-USA from phosphate rock a potential cost effective raw material, by treating with hydrochloric acid.

EXPERIMENTAL

Materials and methods

Analysis of phosphate rock

Phosphate rock was analyzed for determination of phosphorus, fluorides, barium, iron, aluminium, lead, arsenic, chlorides and sulphates contents before its reaction with hydrochloric acid for preparation of dicalcium phosphate dihydrate. The analysis results (measurements made as five replicates) are presented in Table 1.

Collection of samples

Samples of phosphate rock were collected from different origin of Khyber Pakhtoon Khah (KPK) province of Pakistan.

Preparation of samples

The phosphate rock samples were grinded to form powder and pass through 60 mesh sieve and digested in hydrochloric acid to get filtrate before analysis.

Reagent and chemicals

Hydrochloric acid (Merck, Germany), Phosphorus standard 1 mg/mL (Thermo Scientific, USA), Multi-Element Standard (Arsenic, Barium, Iron and Lead 1 mg/mL) (Merck, Germany), Fluoride Standard 1 mg/mL (Thermo Scientific, UK), Mercury (II) thiocyanate (Merck, Germany), Ammonium iron (III) sulphate (Merck, Germany), Nitric acid (Merck, Germany), Ethanol (RDH, Germany) Sodium chloride (Merck, Germany), Potassium hydrogen phthalate (Merck, Germany), Barium chloranilate (Merck, Germany), Potassium sulphate (Merck, Germany), distilled water prepared in our own laboratory.

Instrumentations

Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

All the samples were digested, extracted and run on ICP-OES Model VISTA MPX CCD Simultaneous. Work sheets were prepared with selection of appropriate wavelengths for individual elements: Phosphorus 213.618 nm, Arsenic 188.980 nm, Barium 455.403 nm, Iron 238.204 nm, Lead 220.353 nm, Calcium 396.842 nm, Aluminium 308.215 nm, Magnesium 279.071 nm.

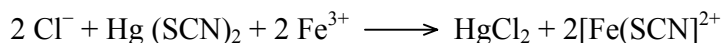
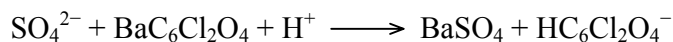
Ion selective electrode (ISE)

Analyses of all samples filtrate for fluoride were performed using Orion 5 Star, Thermo Scientific, USA with fluoride ion selective electrode.

UV-Vis Spectrophotometer

Analysis of all samples filtrate for sulphate and chloride were performed using UV-Vis Spectrometry. The reaction of barium chloranilate and sulphate ion in acidic solution gave barium sulphate and the acidic chloranilate ion. The amount of acid chloranilate ion ($\lambda_{\max} = 530$ nm) liberated is proportional to the sulphate-ion concentration. The amounts of chloride ion depends upon the displacement of thiocyanate ion from

mercury (II) thiocyanate by chloride ion; in the presence of iron (III) ion a highly colored iron (III) thiocyanate complex ($\lambda_{\text{max}} = 460 \text{ nm}$) is formed, and the intensity of its colour is proportional to the original chloride ion concentration.



Synthesis of dicalcium phosphate (DCP)

100 g of powdered phosphate rock was treated with 350 mL, 10% (w/w) hydrochloric acid in a 1000 mL beaker. Reaction mixture was stirred continuously for 2 hrs at room temperature. After reaction the mixture was filtered through sintered glass crucible porosity No. 2 using a filtration flask. Residue was washed with distilled water and washing was collected along with filtrate. To remove impurities like Fe, F, Mg, Al, Pb, As. Calcium hydroxide slurry of 200 mesh sieves was slowly added to the filtrate with continuous stirring in order to adjust the pH at 2.5. Precipitation of impurities occurs at this pH. The mixture was again filtered to get filtrate containing mono-calcium phosphate (MCP). The pH of filtrate was adjusted to 5.0 by addition of calcium hydroxide slurry and precipitates of DCP formed. The precipitates were filtered and washed three times with 100 mL aliquots of distilled water to remove any soluble impurities like chlorides. Then the precipitates were dried at 105°C for 1½ hrs. Di-calcium phosphate dihydrate was grinded to form powder.

RESULTS AND DISCUSSION

Optimum conditions for synthesis of dicalcium phosphate (DCP)

In order to have optimum conditions for synthesis of DCP, different reactions were carried out by changing one parameter at a time and keeping the other parameters constant, like acid concentration, reaction time, reaction temperature, pH at different stages such as during the precipitation of impurities and DCP.

Effect of hydrochloric acid concentration

100 g of powdered phosphate rock was treated separately with different concentrations of hydrochloric acid 5%, 8%, 10 %, 12% and 14%, respectively in a 1000 mL beaker keeping all other parameters constant. 350-550 mL of the above mentioned concentration of hydrochloric acid was used for each reaction. Results of DCP obtained from these reactions are given in Table 2.

Table 1: Analysis of phosphate rock

Samples	Parameters										
	Phosphorus (%)	P ₂ O ₅ (%)	Calcium (ppm)	Fluorides (ppm)	Magnesium (ppm)	Iron (ppm)	Aluminium (ppm)	Lead (ppm)	Arsenic (ppm)	Chlorides (ppm)	
Sample 01	12.11	27.73	21.7	120.4	3700	5900	3200	170	8.93	780	
Sample 02	12.75	29.20	29.7	110.8	3800	4800	3600	120	6.95	890	
Sample 03	12.40	28.40	24.0	104.5	5700	5200	2800	108	6.94	760	

Table 2: Results of DCP synthesized using different concentrations of HCl

HCl (%)	P (%)	% Purity of DCP	Dicalcium phosphate results (n = 5)										
			Ca (%)	SO ₄ ²⁻ (%)	F ⁻ (ppm)	Fe (ppm)	As (ppm)	Pb (ppm)	Al (ppm)	Cl ⁻ (ppm)	Ba (ppm)	Mg (ppm)	
5.0	16.20	90.00	22.78	0.312	110.01	302.11	7.48	22.01	5.64	290.12	9.10	170.09	
8.0	16.90	94.00	26.68	0.367	80.03	310.32	6.12	27.03	5.09	240.09	8.08	168.23	
10.0	17.70	98.20	23.78	0.301	80.01	360.22	3.40	22.01	5.03	240.09	5.04	155.65	
12.0	17.69	98.18	22.98	0.302	70.02	510.32	6.33	28.04	5.26	290.02	9.08	160.08	
14.0	17.70	98.20	22.87	0.367	70.03	586.64	6.58	26.09	5.18	280.03	9.10	177.81	

Effect of reaction/dissolution time

Reaction of phosphate rock was carried out by varying the reaction time ($\frac{1}{2}$ hr, 1 hr, $1\frac{1}{2}$ hrs, 2 hrs and 4 hrs, respectively) and keeping all other parameters constant. For each reaction 100 g of powdered phosphate rock was treated with 400 mL, 10% hydrochloric acid in a 1000 mL beaker at room temperature. Results of DCP obtained from these reactions are presented in Table 3.

Effect of reaction temperature

100 g of phosphate rock powdered was treated with 400 mL, 10 % hydrochloric acid in a 1000 mL beaker at different temperatures (20°C, 25°C, 30°C, 35°C and 40°C respectively) while other parameters remain constant. Reaction mixture was stirred continuously for $1\frac{1}{2}$ hrs. Results of DCP obtained from these reactions are given in Table 4.

Effect of pH at different stages

During synthesis of DCP there are two steps where the pH was adjusted to desired value. The effect of change of pH at these steps was also studied.

Effect of pH during precipitation of impurities

The reaction of phosphate rock was carried out with 400 mL, 10 % hydrochloric acid for $1\frac{1}{2}$ hrs with continuous stirring at room temperature. The mixture was filtered and filtrate was divided into five equal portions. The pH of each portion of filtrate was adjusted to 1.8, 2.0, 2.4, 2.7 and 3.0 respectively using calcium hydroxide slurry. Impurities such as F, Fe and Al were precipitated as Na_2SiF_6 , FePO_4 and AlPO_4 , respectively. The results of DCP at different pH are presented in Table 5.

Effect of pH during synthesis of DCP

At room temperature reaction of phosphate rock was carried out for $1\frac{1}{2}$ hrs in 400 mL, 10% hydrochloric acid with continuous stirring. The mixture was filtered and pH of filtrate was adjusted to 2.4. Precipitates were formed and filtered through sintered glass crucible and pH of five different portions of filtrate was adjusted to 4.0, 4.5, 5.0, 5.5 and 6.5, respectively with calcium hydroxide slurry. The results of DCP obtained from above portions are given in Table 6.

During experimental work dicalcium phosphate (DCP) was synthesized by various procedures to find out the optimum conditions at which best quality of the product can be achieved with maximum yield and minimum cost.

Table 3: Results of DCP synthesized at different reaction/dissolution time

Reaction time (hrs)	P (%)	% Purity of DCP	Dicalcium phosphate results (n = 5)									
			Ca (%)	SO ₄ ²⁻ (%)	F ⁻ (ppm)	Fe (ppm)	As (ppm)	Pb (ppm)	Al (ppm)	Cl ⁻ (ppm)	Ba (ppm)	Mg (ppm)
0.5	16.90	94.00	22.78	0.312	110.09	322.33	7.11	31.09	5.63	270.92	9.09	172.09
1.0	17.30	96.10	26.68	0.367	90.02	334.42	6.43	26.03	5.61	230.08	9.02	188.23
1.5	17.70	98.22	23.88	0.301	80.02	360.73	3.40	22.01	5.09	240.06	5.01	154.05
2.0	17.69	98.18	22.98	0.302	80.03	601.93	6.08	29.81	5.23	270.09	7.06	166.02
4.0	17.70	98.20	22.87	0.367	80.03	723.44	6.28	29.07	5.11	240.07	8.09	167.81

Table 4: Results of DCP on different reaction temperature

Reaction Temp. (°C)	P (%)	% Purity of DCP	Dicalcium phosphate results (n = 5)									
			Ca (%)	SO ₄ ²⁻ (%)	F ⁻ (ppm)	Fe (ppm)	As (ppm)	Pb (ppm)	Al (ppm)	Cl ⁻ (ppm)	Ba (ppm)	Mg (ppm)
20.0	17.70	98.22	22.78	0.312	70.09	281.09	7.11	31.10	5.61	290.18	9.01	182.19
25.0	17.71	98.24	26.68	0.367	80.03	325.02	7.45	29.08	5.43	270.32	8.20	164.23
30.0	17.70	98.26	23.78	0.304	80.06	358.22	3.42	22.03	5.03	241.01	5.09	156.15
35.0	14.40	80.00	22.98	0.302	90.04	508.37	7.89	23.02	5.96	280.03	8.20	163.38
40.0	14.00	78.00	22.87	0.267	90.06	610.32	8.25	22.01	5.09	240.81	8.60	179.31

Table 5: Results of DCP synthesized after precipitation of impurities at different pH values

pH	P (%)	% Purity of DCP	Dicalcium phosphate results (n = 5)									
			Ca (%)	SO ₄ ²⁻ (%)	F ⁻ (ppm)	Fe (ppm)	As (ppm)	Pb (ppm)	Al (ppm)	Cl ⁻ (ppm)	Ba (ppm)	Mg (ppm)
1.8	17.30	96.00	25.78	0.312	100.02	1680.11	7.10	31.08	5.61	290.02	8.12	175.49
2.0	17.50	97.10	26.68	0.367	90.31	1160.23	7.42	29.02	5.43	260.03	8.11	169.82
2.4	17.70	98.20	23.78	0.307	80.02	361.32	3.43	22.12	5.04	241.03	5.02	155.09
2.7	17.67	98.12	22.98	0.302	80.35	315.44	7.83	33.23	5.92	231.03	8.13	162.27
3.0	17.68	98.14	22.87	0.267	70.09	303.92	8.21	22.28	5.01	242.11	8.51	179.11

Table 6: Yield of DCP at different pH values

Yield of DCP (%)	P (%)	% Purity of DCP	Dicalcium phosphate results (n = 5)									
			Ca (%)	SO ₄ ²⁻ (%)	F ⁻ (ppm)	Fe (ppm)	As (ppm)	Pb (ppm)	Al (ppm)	Cl ⁻ (ppm)	Ba (ppm)	Mg (ppm)
44.86	17.64	97.90	22.78	0.312	70.02	386.66	7.11	41.02	5.62	290.23	8.09	180.22
51.00	17.66	98.00	26.68	0.367	80.10	364.54	7.04	29.08	5.04	260.11	9.01	162.23
54.70	17.68	98.10	23.78	0.301	80.01	341.33	3.41	32.21	5.33	231.03	5.02	155.43
62.31	17.70	98.20	23.98	0.302	80.01	362.44	3.40	22.21	5.03	242.02	5.03	164.48
65.11	17.37	96.40	22.87	0.267	80.04	328.32	8.22	32.09	5.08	241.33	8.18	179.61

From the results, it is clear that increase in concentration of hydrochloric acid gradually from 5 to 14% the purity of DCP increases markedly. By increasing hydrochloric acid concentration the amount of fluoride decreased (110.01-70.03 ppm) and the amount of iron increases (302.11-586.64 ppm) in DCP. The optimum HCl concentration was found to be 10%. The purity of DCP increases as the reaction time is gradually increased from ½ - 1½ hrs but on further increasing the reaction time up to 4 hrs the purity of DCP remains constant. The optimum reaction time was found to be 1½ hrs. On increasing the reaction time the amount of fluoride ion decreases first upto 1½ hrs and then becomes stable (80.03 ppm) but the amount of iron increases (322.33-723.44 ppm) in DCP. The purity of DCP remains stable when reaction temperature is increased from 20°C to 30°C and on further increasing the temperature upto 40°C the purity of DCP rapidly falls (78%). The optimum reaction temperature was found to be 30°C. As the temperature of reaction kept high the amount of fluoride ion increased slightly (80.06-90.06 ppm) and amount of iron also increased (381.09-610.32 ppm) in DCP. During precipitation of impurities as the pH is increased from 1.8 to 2.4 the purity of DCP is increased and on further increasing the pH upto 3.0 no significant change occurred in the purity of DCP. The optimum pH value was found 2.4. At this step as the pH increases the amount of fluoride (100.02-80.02 ppm) and iron decrease (1680.11-303.92 ppm) in DCP and other impurities like magnesium and aluminium removed as a result of co-precipitation with calcium fluoride. During synthesis of DCP as the pH is increased from 4.0 to 5.5 the purity of DCP increases and on further increase in pH upto 6.5 the purity of DCP decreases due to the excess of "Calcium" addition in it. The optimum pH value was found 5.5. Increase in pH at this step has no significant effect on the amount of fluoride ion (80.02 ppm) whereas the amount of iron decreases (386.66-328.32 ppm) in DCP.

CONCLUSION

The results of purity of DCP and impurities present in it showed that best quality product with maximum yield can be achieved when different parameters are controlled at optimum values. These optimum values were hydrochloric acid 10%, reaction time 1½ hrs and temperature 30°C, pH 2.3-2.4 during precipitation of impurities and 5.5-5.6 for the final synthesis of dicalcium phosphate. If any of the above parameters changed the quality, yield or both will be affected.

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