Removal and recovery of nutrients as organic fertilizer "solid washed" and inorganic fertilizer "Struvite" from raw and dried poultry manure

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Abstract: Environmental agricultural protection is a concern due to the increase and poor exploitation of poultry manure. Two processes: (1) Thermal treatment and (2) quick wash were investigated to conserve the organic and mineral nutrients. The thermal treatment consists to minimize the weight and reduce the cost of preservation. The chemical treatment consists of a selective dissolution of phosphorus (P) with the most efficient acid from dried and wet poultry manure. Laboratory-scale trials have confirmed that the drying process is useful for reducing 85% total mass and has a disadvantage such as losing 38% nitrogen to air and 36% orthophosphorus in the liquid fraction which is a responsibility to runoff in water. The comparison between the inorganic acid (sulfuric, perchloric and Hydrochloric acid) and the organic acid (acetic acid) was carried out to dissolve more than 90% of P at pH 4.5 with all acids. The performance of sulfuric acid was confirmed; a small amount was consumed and the acid less expensive than the other acid. The centrifugation technique was tested by the reduction of 44% sulfuric acid with the same P extraction performance. As a result of P fresh manure extraction technique, two by-product are produced as organic fertilizer "solid washed" and inorganic fertilizer "struvite".

Keywords: Poultry manure, Organic fertilizer, Phosphorus, Acids, Struvite.

INTRODUCTION

In recent years, the size of poultry has been increased which induces special problems in terms of manure management. In Tunisia, the National Waste Management Agency (NWMA) showed that the amounts of organic waste produced nationally exceeded 8 million tons/year, with the exploitable potential of poultry liquid and solid manure about 378 000 and 226 000 t/year; respectively [1]. The improperly managed manure can degrade the environment quality through ammonia (NH_3) losses that contribute to odor problems and to affect the quality of surface water and groundwater resources by the increases of acid rain[2]. In a way that emissions of NH_3 from agricultural activity and slurry stores represent up to 80% of the total NH_3 emissions of agricultural activities. Moreover, the manure is charged in pathogenic bacteria mainly the staphylococcal (114.10^8 CFU/g) and antibacterials 154.10^6 (CFU/g) which can affect animal productivity [3]. Dramatic advancements are required to protect the environment and save the vital poultry industry and maintain food security. Otherwise, poultry manure can be a valuable resource of organic fertilizer. Nutrients in manure are not provided at the same proportion need by crops, and when manure is applied based on a crop's nitrogen requirement, excessive phosphorus is applied and imbalanced C/P and N/P are recorded, resulting in phosphorus accumulation in soil, phosphorus runoff, and eutrophication of surface waters [2].

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Economical technologies for phosphorus recovery from sludge are yet uncertain [4,5]. Therefore, alternative treatment technologies are required to help manage the large amounts of the generated manure. Treatment processes fall into three categories; physical, chemical; and biological or combination of two or three processes [6]. In this context, it has been reported that the reuse of the recovered phosphorus from animal waste could substitute about 25% of the phosphorus obtained from mining [7]. Therefore, manure management may help to improve the physical and chemical properties of the waste, solve the odor problem, recover nutriment or energy from manure, increase the fertilizer value and reduce its volume and phytotoxicity [8].

Poultry manure as a renewable resource, if managed properly, can serve as a raw material for fertilizer industry [9]. In addition, the depletion of the mineral phosphate resources is a problem that demands special attention in the near future [10]. The sustainable use of phosphorus must include recovery of phosphorus from municipal wastewater, industrial wastewater, anaerobic digester (AD), livestock manure and urine and subsequently using it as a fertilizer [11]. Previous research efforts on phosphorus removal from livestock manure using chemical precipitation have been frustrated due to the large chemical demand and the limited by-products value such as alum sludge flocculation and sedimentation of solids using polymer additive, ozonation, mixing, aeration, and filtration[12]. Moreover, huge losses of ammonium at high pH values have been generated to precipitate phosphorus with calcium (Ca) and magnesium (Mg) salts[13].

There are many studies focusing on the removal and recover of nitrogen (N) and phosphorus (P) from wastewater, such as, swine wastewater [15,16,17] sewage sludge[18] dairy wastewater [19,20], digester supernatant[21,22] and poultry manure [23,24,25]. However, poultry manure wastewater can be successfully pretreated to recover high strength of ammonium nitrogen (85.4% at pH 9.0) by means of high-rate anaerobic digester (AD) to generated energy[24,26].

Moreover, most of poultry manure has been used in co-digestion at different proportion with other waste organic source to enhanced methane yield of digestion [27,28,29].

Environmental requirements imposed post-treatment for digestive to minimize pathogens and recover nutriment [30]. Chemical process has been reported to be beneficial, feasible and advantageous process in the treatment and disposal of poultry wastes [27]. Chemical treatment is a complex process requiring careful operation and several parameters monitoring, such as pH, alkalinity, temperature, stripping hydraulic retention time, stirring speed, organic loading rate and acid quantity and quality.

MATERIALS AND METHODS

1. Poultry manure

Fresh poultry manure samples were collected from a commercial farm housing (10000 poultrys/house) laying hens, located in Borj Cedria, Tunisia. Samples contained feathers and dropped supplies and were not subjected to any treatment on the farm. Poultry manure was subjected to homogenization by hand mixer for 5 min to make uniform in composition, and divided into as many lots of 100 g each as the number of treatments. The sample was kept refrigerated at 4°C until used.

2. Chemical treatment of poultry manure

2.1. Drying effect

The effect of five drying temperature (22, 37, 40, 60 and 105°C) in some tray depth (3 cm) on the manure drying time, drying rate and manure characteristics were investigated. Dried poultry manure was ground and sieved (100µm). Each experiment was performed in triplicate. Samples were left at room temperature for 30 min before the experiment.

Eight tests shall be tested at each the specified temperature and with different levels of pH. Sulfuric acid was the best acid to P extractable (lowers cost and amount) and saving the time and nutriment with drying poultry manure were necessary for acid treatment. When, aqueous solutions of sulfuric acid (H_2SO_4) were added to about 2.0 g of dry manure in a ratio of 1:25 (w/v) at concentration levels of 0, 5, 10, 20, 40, 80 and 160 mM. One experience was tested at pH 8.5 with NaOH (0.1M). The mixture was maintained under magnetic stirring (130 rpm/min) at ambient temperature for 1h (table IV).

2.2. Acids effects

The solid fraction obtained after the drying at open air was subjected to the phosphorus dissolution process prior to the struvite precipitation experiments. Phosphorus dissolution was achieved in four steps: (1) dilution, (2) acidic dissolution, (3) mixing and (4) solid-liquid separation. The aim of which is to facilitate the mixing in the reactor, the solid phase was diluted by distillated water until the total solid TS concentration became 4% (1:25 (w/v)). Then, the pH of the diluted poultry manure was adjusted to around 4.5 by four acids when water was used as reference (Table III).

The sequential extraction scheme described by Szogi et al., (2008a,b) was employed for the fractionation of P into water (H_2O), sulfuric acid (H_2SO_4, 98%), acitic acid ($C_2H_4O_2$, 60%), perchloric acid ($HClO_4$,60%) and hydrochloric acid (HCl, 20%) extractable P. After magnetic stirring for one hour, solid and liquid mixtures were separated by centrifuge (4500 rpm for15min). The liquid supernatant was filtered (Whatman filter paper) and analyzed.

2.3. Thermo chemical and mechanical effect

Table V shows three experiences are carried at pH around 4.5 with aqueous solutions of sulfuric acid addition:

Experience N°1*:* to about 2 grams of dry manure (dried in open air) until the TS concentration became 4%;

Experience N°2: to about 100 g of raw poultry manure untreated when TS= 13% (without water added)

Experience N°3: to about 40g of solid fraction after separation phases of raw poultry manure untreated (TS=10%)

3. Precipitation

The supernatant of the batch experiments was directly used in the struvite precipitation by increasing the pH with controlled amounts of NaOH (0.1M). In order to balance the molar ratios, a quantity of ammonium ($ClNH_4$) and magnesium ($MgCl_2{\cdot}6H_2O$) are added to the solution where P-soluble. The appropriate nutrients weights are calculated according the following formulas [32]:

$$m_{MgCl_2}(mg.L^{-1}) = V(L) \times M_{MgCl_2\cdot 6H_2O(mg.L^{-1})} \times \left(\frac{Mg{:}P \times [PO_4^{3-}](mg.L^{-1})}{M_{P(mg.L^{-1})}} - \frac{[Mg](mg.L^{-1})}{M_{Mg((mg.L^{-1})}}\right) \quad (1)$$

$$m_{ClNH_4}(mg.L^{-1}) = V(L) \times M_{ClNH_4(mg.L^{-1})} \times \left(\frac{N{:}P \times [PO_4^{3-}](mg.L^{-1})}{M_{P(mg.L^{-1})}} - \frac{[NH_4](mg.L^{-1})}{M_{NH_4((mg.L^{-1})}}\right) \quad (2)$$

Where m_{MgCl2} is the mass/weight; V is the volume of (L);M_{ClNH4} is the molar mass of $ClNH_4$

The sample was filtered through membrane filters (pore size of 0.45µm) prior to analysis. Then, the solid was dried at open air.

4. Analytical methods

The determination of PO_4^{3-} concentrations in aqueous solutions was performed using an UV-visible spectrophotometer (Thermo Spectronic UV1 equipped with VISIONlite TM software) at 430 nm. NH_4^+ content was determined by Kjeldahl method [33]. Inorganic phosphorus (Pi) was determined using a modified molybdate blue method [34]. Total phosphorus (P_{tot}) concentrations in manures and extracts were determined by ultraviolet-visible spectroscopy after dry combustion at 550°C and digestion in 0.5 M sulfuric acid (H_2S0_4). Organic phosphorus (P_o) was estimated as the difference between P_{tot} and P_i. The concentrations of Mg^{2+} and Ca^{2+} were determined using the EDTA method[33].

Total solids (TS) and volatile solids (VS) were determined by the method described by APHA, 2005[35].

RESULTS AND DISCUSSION

1.Drying temperature effect

The data on the drying time, moisture content and drying effectiveness at various drying temperatures are presented in Table I. The obtained results show that the poultry manures contained about 10-14% dry matter (DM) when dried at temperature ranging from 22 to 105°C. TS and VS decreased as the drying temperature increases. However, the time is varied between 1 and 11 days with 105°C and open air, respectively. The minimum TS is observed at 37°C (TS= 0.1 g.g^{-1}). This temperature is very favorable for microorganism's growth causing the organic matter degradation and as a result the manure TS was decrease. Furthermore, results show that as higher is the drying temperature (from 22 to 105°C) as more the DM content is altered by the drying procedures. The general trend was that higher drying temperatures (from 22 to 105°C)[36]. Noted that 105°C to open air (22°C) dried samples contained less moisture than manures subjected to other temperature drying but not too much difference was distinguished between samples dried at 37, 40 and 60°C. The original high TS were recorded at the highest temperature of drying process and caused by water molecules intercalated. In addition, a small increase in temperature (37 to 40°C) can be gain

Table I: Effect of time and temperature drying

Temperature of drying °C	Times (days)	TS ($g.g^{-1}$)	VS ($g.g^{-1}$)	Moisture (%)
22(air dried)	11	0.135	0.125	86.5
37	12	0.1	0.0925	90
40	7	0.12	0.111	88
60	2.5	0.125	0.115	87.5
105	1	0.14	0.129	86

M1=200g (fresh manure); M2: dried matter;
M3: mass of matter after dry combustion at 550°C about 5h. TS=M2/M1; VS=(M2-M3)/M1

five days of drying (12 to 7 days). Yet, this observation seems reasonable with the results observed by Dail *et al* [35]. The results obtained from the present study showed the difference in drying time between the manure layers decreased as the temperature increased (12 to 1 days from 22 to 105°C).

In addition. the pH increased by one unit; from 5.53 to 6.66 with raw and dry manure; respectively (Table II). The amount of total Ca. Mg and P in 1 kg TS are not changed in both raw and dry poultry manure (Table II). In contrast, total N content in raw and dry poultry manure recorded a decrease of about 32% to reach 36 and 24.5 $g.Kg^{-1}TS$. respectively (Table II). The phenomenon could be that amount of N in the supernatant reacted with temperature to transformed NH_3 gaz again and decreased pH. As a result, the thermal treatment seems to be effective in reducing odor-generating compounds and microorganisms contained in the manure. In fact, as the drying process progressed. the generated odor is less and less felt and unpleasant odor is detected in the final product (dried manure). In this way fertilizer value of dry manure is improves and ammonia emission is reduced after matter stabilization by temperature drying [37]. The resulted dry matter will be used as basis nutrient contents such as P and N comparison in the different samples.

2. Temperature and pH effects on the P and N content

The drying temperature increase would cause decomposed P to become less H_2O soluble. Such thermal process approves the conservation of the majority of nutriment in solid manure and avoids the runoff. This phenomenon was confirmed by a literature, where it has been shown that the drying process decreased orthophosphate content in poultry manure when pH increased from 5.53 to 6.66 [38]. Table III and Table IV shows the extracted P and N amounts from poultry manure dried at 22; 37; 44; 60 and 105°C using different sulfuric acid concentrations (0-160 mM). Results show that poultry manure has been found to have a little change in H_2O and acid-extractable P and N when drying at all temperature from 22 to 105°C. Besides, when water solution (without acid) is used, around 30 and 40% of P and N are extracted; respectively. By inference, the majority of P in manure is not dissolved. It has been reported that water-extractable P and N in manure are correlated with P and N in runoff from the recently amended soil. which leads to an environment risk increase [39]. During acid extraction, the major portion of total P in pig manure solids was hydrolyzed and transferred into the extract solution [30]. Total P extraction rates increased with increasing acid concentrations [7]. With sulfuric acid, pH values in the range of 5.56 to 4.56 units were recorded when the acid concentrations changed from 5 to 40 mM. These sulfuric acid applied concentrations provided removal rates of 34-87% of the initial P_{tot}. Meanwhile, the control using distilled water extracted only 28% of the initial P_{tot} in manure

Table II: Drying effect of poultry manure on its biochemical composition

Unit	pH	TS ($g.kg^{-1}$)	VS	Moisture (%)	Ptotal ($g.kg^{-1}$)	Mg total ($g.kg^{-1}$)	Ca total ($g.kg^{-1}$)	N-NH_4^+ ($g.kg^{-1}$)
Raw poultry manure	5.53±0.3	137±0.4	126±0.4	86.3±0.4	20.88±0.5	14.83±1	13.79±2	36±12
Dry poultry manure*	6.66±0.1	807±0.8	744±0.6	19.28±0.8	21.16±0.4	15.08±2	14.08±1	24.5±12

*poultry manure dried in open air

Table III: Effect of sulfuric acid/hydroxide sodium treatment on pH extraction. Phosphorus extracted

Treatment	pH mixture	Acid/ Base	Air dry (22°C)		37°C		44°C		60°C		105°C	
			P_extracted									
		mM	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%
1	8.5	0.1	9	1	9	1	10	1	8	1	241	29
2	6.58	0	241	29	276	33	265	31	251	30	241	29
3	5.56	5	291	34	264	31	284	34	280	33	276	33
4	5.31	10	275	33	274	32	286	34	304	36	297	35
5	4.74	20	637	75	647	76	624	74	620	73	610	72
6	4.56	40	740	87	720	85	732	86	714	84	722	85
7	3.35	80	771	91	730	86	774	92	775	92	773	91
8	1.85	160	805	95	785	93	784	93	803	95	821	97

solids. Unlike acid concentrations. the drying temperature (22 to 105°C) seems to have no significant effect on P_{tot} extracted. At double molar concentrations (80 mM), pH was decreased unit to reach 3.35 and extracted P_{tot} was increased by 4%. Whereas, when acid concentration was increased 4 times (160 mM), 1.85 of pH value was reached and 8% of P_{tot} was extracted. In the same way, 85% and 90% of P were released when pH values were at 4.4 and 1.4; respectively [30]. When acid concentration is 40 mM. more intense acidification (pH<4.5) was obtained with all drying temperatures and more than 85% of P_{tot} was extracted. P extraction efficiency is more important when acid molar concentration increases. However, it seems to be not useful to make pH values lower than 4.5, since no P extraction improvement was recorded. This will be exhausted more acid quantity and generate therefore an over P recovery cost. However, pH are adjusted to 2.0 by the addition of 20 % HCl (v/v) [40]. In addition, at pH 4.5, the extracting liquid becomes corrosive and unnecessary oxidation of organic compounds can occur [6]. Otherwise, when basic solution is used (pH 8.5) around 98% of P content remained in the washed manure. The majority of P will be associated with calcium Ca-P. In contrast, almost all the N content (97%) is released in form of NH_3 (gas). The above findings show that at temperatures equal or less than 105°C; ammonium

Table IV: Effect of sulfuric acid/hydroxide sodium treatment on pH extraction. Ammonium-extracted

Treatment	pH mixture	Acid/ Base	Air dry (22°C)		37°C		44°C		60°C		105°C	
			N_extracted									
		mM	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%	mg.L^{-1}	%
1	8.5	0.1	25	3	35	4	45	5	28	3	33	3
2	6.58	0	364	37	355	37	355	37	355	37	390	40
3	5.56	5	371	38	350	36	359	37	359	37	395	41
4	5.31	10	368	38	350	36	350	36	350	36	356	37
5	4.74	20	366	38	358	37	360	37	360	37	380	39
6	4.56	40	375	39	345	35	365	38	365	38	385	40
7	3.35	80	383	39	348	36	358	37	368	38	370	38
8	1.85	160	376	39	350	36	345	35	355	37	375	39

Table V: Natural of acid effect when poultry manure dried at 22°C.

Acid	pH	quantity of acid		Ca^{2+}	Mg^{2+}	P	N
Unit		Kg.Kg^{-1} P	Kg.m^{-3}	mg.L^{-1}	mg.L^{-1}	mg.L^{-1}	mg.L^{-1}
Water (control)	6.66±0.1	3344.13±2	1000±1.1	31.7±10.4	64±6.9	299.03±17.8	363.97±6.6
Sulfuric	4.44±0.1	3.52±0.12	2.56±4.4	346.37±30.6	468±12	728.41±24.6	371.65±7.9
Perchloric	4.45±0.1	15.75±0.25	11.69±1.3	366.37±20.8	460±38.6	742.40±11.6	374.68±7.5
Chloric	4.38±0.1	19.18±0.1	14.28±1.3	336.67±15.3	468±21.1	744.40±33.9	389.83±22.4
Acetic	4.27±0.2	35.7±1.2	25.75±2.5	351.37±23.6	412±18.3	721.18±24.7	363.49±3

and orthophosphate removal by chemical yields important rates. Such results were confirmed; where the treatment process was conducted at temperature values ranging from 5 to 50°C [8]. In addition. drying temperature could be increased to 105°C to decrease duration of drying poultry manure (Table I). However, drying poultry manure at open air might have as much as three times more nitrogen content than composted poultry manure content [41]. In addition, composting ensures potential pathogens mortality such as *Salmonella*. stabilizes the organic matter with a high degree of humidity and improves its quality as a soil amendment [41].

3. Acid nature effect

Sulfuric, Perchloric, Hydrochloric and Acetic acid were used separately the aim to dissolve the mineral phosphorus in dried poultry manure. Sulfuric acid is cheaper and more efficient than the others acids [42]. HCl and $HClO_4$ are strong inorganic acids and acetic acid is a weak organic acid. Although that it has been demonstrated that the formic acid is more efficient for P extraction than the acetic acid [43]. In this study, the acetic acid which is more available and low-cost in Tunisia was used. The obtained results in terms of the matrix composition are illustrated in (Table V). The required amounts of inorganic and organic acid to reach around 1 Kg of P extracted were very different between organic and inorganic acids, also between the strong and weak inorganic acids. Then, to dissolve 1 kg P, the amount of sulfuric, perchloric, chloric and acetic acid were 3.52. 15.7. 19.2 and 35.8 Kg; respectively.

The results show the concentrations of nutriments after 11 days of drying the poultry manure at room temperature. The residual matter removals of the products obtained using sulfuric. perchloric. hydrochloric and acetic acid were 33.3, 32.7, 30.4 and 34 %. Respectively (Table VI). The total amounts of calcium, magnesium and phosphate ammonium in the supernatant were comparable for all the used acids at pH 4.5. The extracted total phosphorus using water is about 36% versus 87% using acids. However, no difference is noticed in terms of N extracted with both (about 38%).

There was more difference between the four treatments in terms of quantities of acid addition. Acids performances in terms of P_extracted from dry poultry manure could be ordered as follow: sulfuric > perchloric > chloric > acetic > H_2O (Table VI). The P distribution as reported by different authors may be due to animal diets.

Table VI: Natural of acid effect at pH 4.5±0.1 when poultry manure dried at 22°C**.**

Acid	P_extracted %	N_extracted %	N:P residual	residual removal %
Water (control)	35.80±2.13	37.14±0.67	1.15±1.19	29.95±4.51
Sulfuric	87.21±2.95	38.23±0.81	5.70±1.2	33.33±1.13
Perchloric	88.89±1.4	39.77±2.28	6.52±1.18	32.73±0.71
Chloric	89.13±4.06	39.78±2.28	6.50±1.19	30.38±4
Acetic	86.35±2.96	37.09±0.31	5.41±1.2	34.03±1.53

specially the level of mineral supplementation. The amount of sulfuric acid needed to dissolve 1 Kg of phosphorus in poultry manure is half of the quantity extracted from poultry litter (7 $Kg.Kg^{-1}$) [6]. Thus, this amount was 20 folds more than the required amount of hydrochloric acid (0.9$Kg.Kg^{-1}$) to dissolve phosphorus in the wastewater sludge ash [43]. The amount of acid depends strongly on the concentration of the inorganic and organic elements in samples. In addition. it also depends on the initial concentration of the commercial acid. The acid content necessary to lower the pH is proportional to the level of organic and inorganic matter. In a previous work, it has been reported that 20 Kg of acetic acid were required to dissolve 0.832Kg of P in 1 m^3 of pig slurry supernatant where TS=64±3$g.Kg^{-1}$; the equivalent of 24Kg acetic acid. Kg^{-1}P [42]. In the present study, 35.6 Kg of acetic acid was needed to dissolve 1 Kg of P and around 39 Kg acetic acid in 64 kg TS of dry poultry manure. As a result, to obtain 1kg P extracted, 77 kg of TS in the pig slurry is required versus only 55 kg of poultry manure in this work. The washed residue resulted from this treatment ended with a N:P ratio around 6 with all the used acids (Table VI). This N:P ratio was 5.4 fold higher than the N:P ratio of the untreated poultry manure (N:P = 1.15). Those values are ranging in the required balanced fertilizer standards (3.3-16.7) for typical crops and pastures [6,44]. It's worthy to remind that the initial N:P ratio of the untreated poultry manure was imbalanced which may cause serious damage to the environment. The acid quick wash process has corrected this ratio by removing the majority of organic P and leaving the half of N in the washed residue with a more favorable N:P ratio to make a suitable washed manure for crop production [6].

4. Thermo-chemical and mechanical effects

Previous studies have yielded conflicting results on the effect of drying on H_2O-extractable P in manures and it appears that P solubility is related to specific manure chemical physical characteristics [43]. During thermal treatment, the manure pH increased from 5.6 of fresh samples to reach 6.7 of the dried ones. The increase in pH

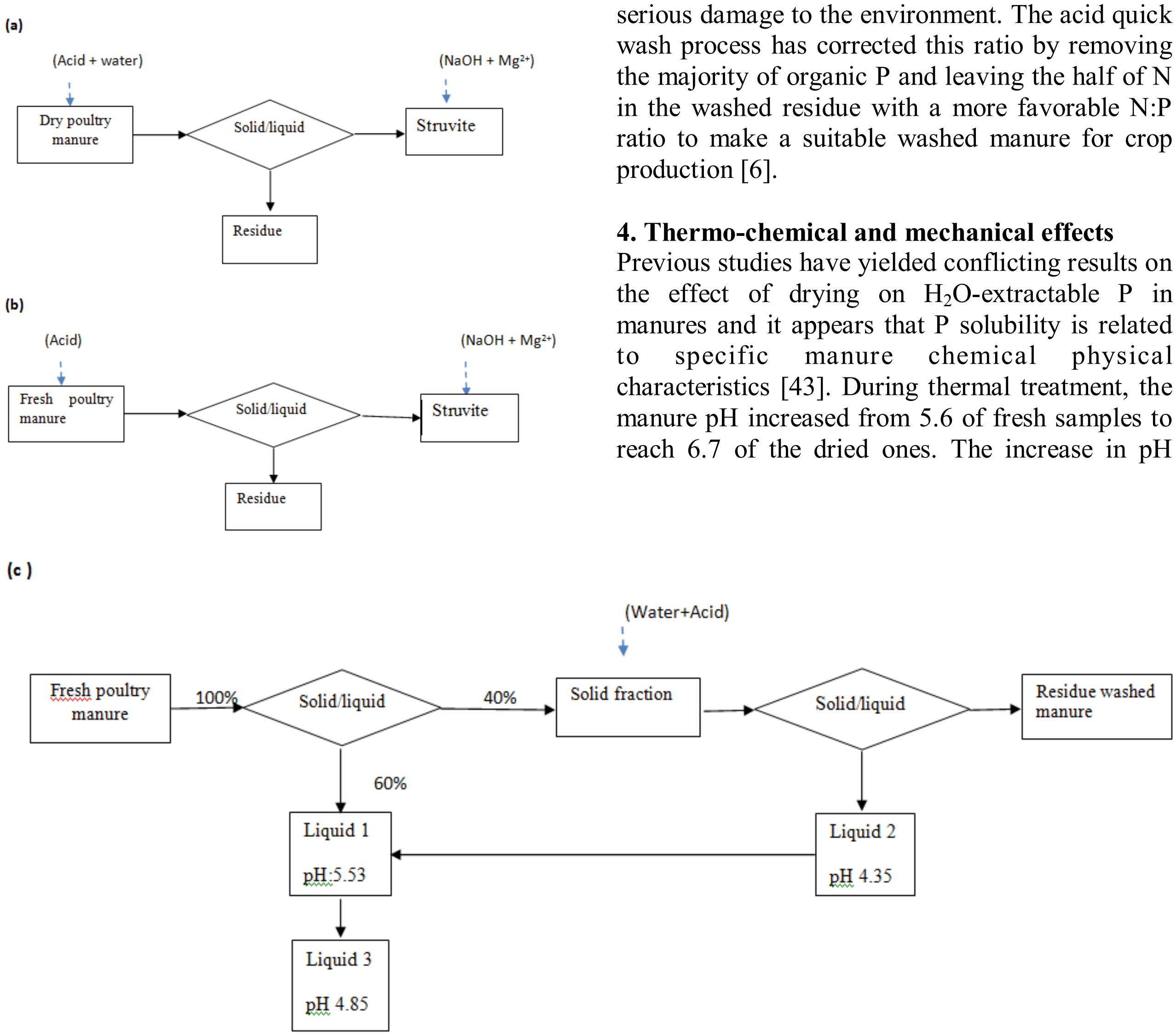

Figure 1: Technical schematic of the combined mechanical and phosphorus removal treatment by acid addition to pH 4.5; **(a)** in dry poultry manure; **(b)** in raw poultry manure: **(c)** in solid fraction after centrifugation.

Table VII : Thermo-chemical and mechanical process combined to removal phosphorus

Acid	pH	Quantity of acid	P_extracted	N-NH$_4$	N_extracted	N:P residue
		Kg.Kg^{-1} P	%	mg.L^{-1}	%	
H2O	6.66±0.07	0	35.8±2.13	363.97±6.62	37.14±0.67	1.15±1.2
Dry manure	4.44±0.1	3.52±0.12	87.21±2.95	371.65±7.93	38.23±0.81	5.7±1.2
Raw manure	4.45±0.25	2.29±0.05	88.03±2.3	540±5	38.55±0.34	10.2±0.03
After centrif :						
Solid fraction	4.5±0.1	1.97±0.05	57.5±1.2	245.42±5.2	17.04±0.36	10.28±2.6
Liquid fraction	5.53±0.1	0	30.67±0.5	285.33±5	19.81±0.35	nd

with drying temperature could be attributed to the associated of orthophosphate with Calcium; Ca-P precipitation process. Opposite results were reported by other researchers at basic conditions. When drying poultry manure for pelletizing as fertilizer, pH is dropping from 8.5 to 7.9 [45]. Also, the literature noticed lower pH values for dried poultry manure compared to initial values [46]. The decrease in pH with drying temperature could be attributed to the loss of ammonium through the volatilization process at pH>8.

Recently, recovery of P from waste can be grouped into two types of processes: (1) recovery of the liquid phase [6] and (2) recovery of the solid phase such as sludge ash [47], dried litter manure [8] and fresh pig manure solid [6]. In order to minimize acid consumption, this study approach is carried out on dried manure, in the open air, and with fresh poultry manure with moisture content of 19 and 86%; respectively. In addition, another comparison of acid consumption was carried out with a mechanical separation of two phases (Figure.1).

4.1. Comparison between dry and fresh poultry manure

The necessary amount of sulfuric acid to recover 1 kg P is 3.5 and 2.3 kg H_2SO_4 from dried (1:2w/v) and fresh (without dilution) poultry manure; respectively. pH value reached 4.5. A reduction of 35% in acid consumption and 1.3m^3 in water dilution were obtained. Moreover. gain in space and drying time could be achieved when fresh manure is used.

4.2. Comparison between solid and liquid fraction from fresh poultry manure

Fresh manure was centrifuged to separate solid and liquid phases in order to minimize the concentration of the minerals before the addition of acid. Results show that almost 1/3 of the P was recovered in the manure liquid phase (Table VII).

The quick wash process was carried out on the solid phase after centrifugation (40% of the initial mass) and after dilution (1: 1 (w / v)) (Figure 1- c). After second separation. the liquid phases when pH 4.5 are added to the first liquid fraction (initial pH

Table VIII : Thermo-chemical and mechanical process combined to removal phosphorus

	pH	Ca^{2+}	Mg^{2+}	P	N-NH$_4$
		mg.L^{-1}			
H2O	6.66±0.07	31.7±10.4	64±6.9	299.03±17.8	363.97±6.62
dry manure	4.44±0.1	346.3±3	360.3±7.6	746.56±17.9	371.65±7.93
raw manure	4.45±0.25	351.67±3	373.3±5.7	735.23±19.4	540±5
after centrif :					
solid fraction	4.5±0.1	280±10	270.8±5.3	480.38±9.9	245.42±5.2
liquid fraction	5.53±0.1	37.67±2.5	75.17±3.01	256.1±4.2	285.33±5

Table IX : Removal phosphorus and Ammonium as Struvite

Supernatant	*	initial pH	initial Mg:N:P	final Mg:N:P	Ca:P	MgCl2.6H2O mg.L^{-1}	NH4Cl mg.L^{-1}	Recover N (%) struvite	Recover N (%) gas	Recover P (%)
with acid	dry	4.5	0.6:0.9:1	01:01:01	0.36	1843	182	85	10	85
	L2	4.45	0.6:1.3:1	1:1.26:1	0.37	1668	0	72	8	92
	L3	4.85	0.6:1.6:1	1:1.24:1	0.33	1900	0	76	6	95
without acid	L1	5.53	0.4:1.9:1	0.4:1.9:1	0.11	0	0	20	0	38

*dry, L2, L3 and L1 : supernatant in dry manure (figure 1-a) and raw poultry manure figure (1-c); respectively.

5.53). The final pH in liquid fraction are 4.85. For the same purpose, it was found that the amount of acid was decreased to 2 kg/1 kg P. This way can be reduced 14% of acid (Table VII). A comparison can be made of the acid amount used between scenarios (b) and (c) in (Figure 1) i.e. between using removal P without and with mechanical separation in fresh poultry manure, respectively.

4.3. Thermo-mechanical comparison

At pH 4.5. 3.5 and 2 kg of sulfuric acid are needed to dissolve 1 kg P in dry and solid fresh fraction from poultry manure; respectively. The amount of acid and water are decreased to 44 and 70%; respectively (Figure 1-a and c).

In addition, N:P residue are 5.7, 10.2 and 10.28 in dry, raw and raw after centrifugation treatment; respectively. The N:P ration increased with fresh poultry manure. This is explained by the reduction of nitrogen with drying (-35%).

5. Precipitation of struvite

Prior to the struvite ($MgNH_4PO_4.6H_2O$) precipitation experiment. four experiences are affected with TS<4% and different supernatant (Table IX).

5.1 With acid/ base addition

Three supernatants are treated in this comparison:

***Experience N°1**:* Supernatant (a) from dry poultry manure of the optimum condition of removal P; pH 4.5 with sulfuric acid. The concentration on ortho-phosphorus PO_4^{3-}, ammonium NH_4^+, magnesium Mg^{2+} and calcium Ca^{2+} are about 2288, 372, 360 and 346mg.L^{-1}; respectively.

Table IX: Struvite precipitation

However, the initial ration Mg:N:P = 0.6:0.9:1 and Ca:P = 0.36. Crystals of struvite will form when the ration Mg:N:P=1:1:1. According to equation 1 and 2; 1843 and 182 mg.L^{-1} of $MgCl_2{\cdot}6H_2O$ and NH_4Cl are added to achieve this ratio. NaOH (0.1M) is added to pH 9 with a stirring rate 200 rpm for 1h. The removal rates of N and P were 95 and 85%; respectively. A small amount of N (10%) is removed as a gas through a high pH. This result is similar to the findings of several authors. They noted that the recovery percentage of N and P as struvite is very high at pH 9 with equal molar of Mg^{2+}, NH_4^+ and PO_4^{3-}. Furthermore, the removal efficiencies of NH_4–N and PO_4–P were 89.35% and 95% when Mg:N:P molar ratio was 1.5:1:1 and pH was 9.0 [48].

***Experience N°2**:* Supernatant from fresh poultry manure of the optimum condition of removal P; pH 4.5 with sulfuric acid (Figure1-b) and (Table VIII). The ration Mg:N:P=0.6:1.3:1 and Ca:P=0.37, struvite will form when Mg:P≥1. In this case, 1668 mg.L^{-1} $MgCl_2{\cdot}6H_2O$ are added to achieve Mg:P=1. At pH 9; 72% of N and 92 % of P are removed as struvite and 8% of N as gas.

***Experience N°3*:** Supernatant from fresh poultry manure after second separation of the optimum condition of removal P; pH_f 4.85 with sulfuric acid (Figure 1-c). The ration Mg:N:P=0.6:1.6:1 and Ca:P=0.33. Struvite will form when Mg:P≥1. In this case, 1900 mg.L^{-1} $MgCl_2{\cdot}6H_2O$ are added to achieve Mg:P=1. At pH 9; 76% of N and 95 % of P are removed as struvite and 6% of N as gas.

5.2 Without acid/base addition

Experience N°4: Supernatant from fresh poultry manure when pH initial 5.53 without acid and any chemical addition or agitation and pH adjustment (Fig1-c). The ration Mg:N:P=1.5:5.24:1 and Ca^{2+}: PO_4^{3-}=0.35. At a low temperature 5°C and high concentrations of struvite constituent ions. crystal germination will occur on the beaker wall. Analyzes of the supernatants showed the 20% decrease in ammonium, which is the indicator of

struvite formation. However,vStruvite formation is likely dependent on Ca^{2+}:PO_4^{3-}<0.5 [49]. Furthermore, that in a synthetic raw solution, a high N:P ratio(3:1), moderate stirring rate (between 45 and 90rpm) and low temperature (below 20°C) improved the precipitation of struvite [50]. If all ammonium removed from supernatant was attributed to struvite formation, then approximately 38% of orthophosphate was formed as struvite particules. In addition. it can be explained by the increasing germination kinetics at low temperature 5°C for a long time.
After struvite will form when Mg:P≥1. In this case, 1668 mg.L^{-1} $MgCl_2{\cdot}6H_2O$ are added to achieve Mg:P=1. At pH 9; 76% of N and 95 % of P are removed as struvite and 6% of N as gas.

CONCLUSION

The present study investigated the potential for removal and recovery of nutrients by struvite formation from the poultry manure. In the five temperature drying manures tested. the most significant change was observed in air-dried manure with sulfuric acid extracted P and N fraction at pH 4.5.
A supernatant was obtained after "quick wash" with sulfuric acid at a concentration of 80mM (pH <4.5) rich in P. to precipitate the high quality struvite. an amount of N and Mg were added to adjust the molar ratio and to adjust pH to 9 by adding NaOH (0.1).
Drying manure is not recommended; loss of macro -elements and high cost during (waste of time and energy) so the "quick wash" with acid to dissolve the nutrient is more effective in fresh manure. Recovery of N and P from raw poultry manure is an interesting process that can be studied in detail.

REFERENCES

[1] NAWM. **2013**. National Agency for Waste Management.
[2] D. Fangueiro, M. Hjort, F. Gioelli, *J. Environ. Manag.*, **2015**, *149*, 46.
[3] N.Anderson, R.Strader, C.Davidson, *Environ. Int.*, **2003**, *29*, 277.
[4] D.Davelaar, **2007**, Rethinking wastewater biosolids, phosphorus recovery and sustainability.Moving forward: wastewater biosolids sustainability: technical, managerial, and public synergy. In: Proceeding of Specialist Conferences of IWA and WEF. June 24–27, Canada, pp. 867–874
[5] A.A. Szogi, M.B. Vanotti, G.H. Patrick, *J. Environ. Manag.*, **2015**, *157*,1.
[6] A.A. Szogi, M.B. Vanotti, *Bioresour. Technol.*, **2009**, *100*, 5461.
[7] A.A. Szogi, M.B. Vanotti, *J. environ. qual.*, **2014**, *43*, 1219.
[8] F. Oscar, O.F. Schoumans, F. Bouraoui, C. Kabbe, O. Oenema, K. C.van Dijk, *Ambio.*, **2015**, *44*, 180.
[9] K. Yetilmezsoy, F. Ilhan, E. Kocak, H.M. Akbin. I. Emel, *J. Clean. Pro.*, **2017**, *152*, 88.
[10] U.D. Sibel, O. Maazuza, *Bioresour Technol.*, **2009**, *100*, 3236.
[11] Md.M. Rahman, M.A.M. Salleh, U. Rashid, A.Ashan, M.M.Hossain, C.S.Ra, *Arab. J. Chem.*, **2017**, *7*, 139.
[12] M.M. Chirag, O.K. Wendell, N. Vivi, T. Stephan, J.B. Damien, *Crit Rev. Environ. Sci. Technol.*, **2014**, *35*, 385.
[13] P.W. Westermana, J.R. Bicudob, *Bioresour. Technol*,. **2000**, *73*, 1.
[14] Y. Jaffer, T. Aclark, P. Pearce, S.A. Persons, *Water. Res.*, **2002**, *36*, 1834.
[15] N.O. Nelson, L.M. Robert, D.L. Hesterberg, *Bioresour. Technol.*, **2003**, *89*, 229.
[16] K. Suzuki, Y. Tanaka, K. Kuroda, D. Hanajima, Y. Fukumoto, *Bioresour. Technol.*, **2005**, *96*, 1544.
[17] Md.M. Rahman, Y.H. Liu, J.H. Kway, C.S. Ra., *J. Hazard. Mater.*, **2011**, *186*, 2026.
[18] E. Munch, K. Barr, *Water. Res.*, **2001**, *35*, 151.
[19] S.U. Demirer, G.N. Demirer, S. Chen, *Process Biochem.*, **2005**, *40*, 3667.
[20] M.S. Massey, J.G. Davis, R.E. Sheffield, J.A. Ippolito, *ASABE.*, **2007**, *701*, 907.
[21] P. Battistoni, P. Pavan, M. Prisciandaro, F. Cecchi, *Wat. Res.*,**2000**, *34*, 3033.
[22] L. Pastor, D. Mangin, J. Ferrer, A. Seco, *Bioresour. Technol.*, **2010**, *101*, 118.
[23] A.A. Szogi, M.B. Vanotti, P.G. Hunt, *ASABE.*, **2008**, *51*, 1727.
[24] K. Yetilmezsoy, Z.S. Zengin, *J. Hazard. Mater.*, **2009**, 166, 260.
[25] Y.D. Yilmazel, G.N. Demier, *Environ. Technol.*, **2010**, *32*, 783.
[26] K. Yetilmezsoy, S. Sakar, *J. Hazard. Mater.*, **2008**, *151*, 547.
[27] Y.D. Yilmazel, G.N. Demier, *Waste. Manag. Res*, **2013**, *3*, 792.
[28] B. Sebastian, W. Laurence, *Bioresour. Technol.*, **2013**, 142, 345.
[29] K. Sonia, A. Louhichi, S. Sayadi, *Bioresour. Technol.*, **2015**, *182*, 67.
[30] Y.D. Yilmazel, G.N. Demier, *Environ. Technol*, **2011**, *32*, 783.
[31] Elsie Maria, **2011**, Development of an aerated struvite crystallization reactor for phosphorus removal and recovery from swine manure. Canada. pp. 35.
[32] J. Rodier, **2009**
[33] Z. He, C.W. Honeycutt, USDA-ARS., **2005**, 536.
[34] APHA. AWWA. WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed.,

Washington, DC, **2005**.
[35] H.W. Dail, H. Zhongqi, M.S. Erich, C.W. Honeycutt, Commun. Soil. Sci. Plant. Anal., **2007**, *38*, 1879.
[36] A.M. Chaudhry, E.B. Barbier, IAAE., **2013**, *44*, 175.
[37] Z. He, B.J. Cade Menun, G.S. Toor, A.M. Fortuna, C.W. Honeycutt, J.T. Sims, *J. enviran. Qual*., **2007**, 36, 1086.
[38] P.J.A.Kleinman, A.M.Wolf, A.N.Sharpley, D.B. Beegle, L.S.Saporito, S.S.S.A.J., **2005**, 69, 701.
[39] M.L. Daumer, F. Beline, F. Guiziou, M. Sperandio, *Biosyst. Eng*., **2007**, *96*, 551.
[40] C. Mondini, R. Chiumenti, F. da Borso, L. Leita, M. De Nobili, *Bioresour. Technol*.,**1996**, *55*, 243.
[41] A.A. Szogi, M.B. Vanotti, P.G. Hunt, **2008**, ASABE, *51*, 1727.
[42] M.L. Daumer, S. Picard, P. Saint-Cast. P, Dabert, *J. Hazard. Mater*, **2010** ,*180*, 361.
[43] T. Dockhorn, **2009**, About the economy of phosphorus recovery. In: International Conference on Nutrient Recovery from Wastewater Streams, *IWA Publishing*, London.
[44] W. Zhang, A. Lau, *J. Chem. Technol. Biot*., **2007**, *82*, 598.
[45] M.E.L. Mosquera, E.F. Cabalerio, M.J. Sainz, A.L0 Fabal, E. Carral, *Bioresour. Technol*., **2008**, *99*, 5626.
[46] O. Dikinya, N. Mufwanzala, *J. Soil. Sci. Environ. Manage*., **2010**, *1*, 46.
[47] E. Desmidt, K. Ghyselbrecht, Y. Zhang, L. Pinoy, B. VanderBruggen, W. Verstraete, K. Rabaey, B. Meeschaert, *Crit. Rev. Env. Sci. Technol*., **2015**, *45*, 336.
[48] A. Uysal, Y.D. Yilmazel, G.N. Demirer, *J. Hazard. Mater.*, **2010**, *181*, 248.
[49] W. Tao, A.T. Ukwuani, *Chem. Eng. J*., **2015**, *280*, 188.
[50] A. Capdevielle, S. Eva, B. Beatrice, B. Fabrice, M.L. Daumer, *J. Hazard. Mater*., **2013**, *244*, 357.