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Phosphorus Extraction from Fish Waste Bones Ash by Acidic Leaching Method

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Abstract: The worldwide demand of phosphorus (P) is rising rapidly; however phosphate ores are not renewable. Fish bones contain high amounts of P, but hardly recycled or reused. Therefore, this study investigated P extraction from fish waste bones by acidic leaching method. The study shows that P content in fish bones ash is around 17 wt.%. Acidic leaching of P is carried out using different concentrations of sulphuric acid (H_2SO_4), to determine the optimum condition of P recovery. More than 97% of P is extracted using 2 M H_2SO_4 and an acid-ash ratio of 1.5 kg H_2SO_4/kg ash. Besides, it was found that a reaction period of 90 min is enough to accomplish complete dissolution of fish waste bones ash. The present work suggested that recovering P from fish bones ash is worthy, which is highly advantageous for further applications that apply P additions.

Key words: Phosphate, fish bones ash, sulphuric acid, phosphorus recovery.

Introduction

Phosphorus (P) is one of the most vital elements that is necessary for agricultural and industrial applications. Basically, P is an essential nutrient for most organisms in the ecosystem, and cannot be replaced by any other element. Moreover, it is a fundamental element for many industries such as food and fertilizers. The global demand of phosphate rock has increased by an average of 4.44% per year in the decade of 2006 to 2016, which is the highest level in history (Vaccari et al., 2019). Besides, P is a non-renewable source that is considered a cost-saving commodity; however its market value does not account for its insufficiency (Theregowda et al., 2019). So, in order to maintain sustainable environmental management, recycling and reuse of P is of great importance.

Normally, P compounds exist in many kinds of wastes such as wastewater sludge (Quist-Jensen et al., 2018) and organic wastes (Schoumans et al., 2015). Specifically, organic wastes contain considerable amounts of P; however this kind of waste is often

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disposed directly to landfills, or after incineration (in the form of ash), which is hardly usable or utilized. Different methods have been introduced to extract P from incinerated wastes ashes. The basic approach of these methods is the dissolution of P in an acidic or alkaline media, followed by a selective chemical and/or physical separation process. The dissolution of P from ash is a necessary step, which is influenced by different factors such as type and strength of separation media (acid or base) and the chemical characteristics of the ash.

Extensive research work has been conducted to determine the optimum condition for P dissolution from several ash types. Petzet et al. (2012) investigated P extraction from sewage sludge ash using a sequential treatment method with an acid (HCl) and a base (NaOH). The authors revealed that their methodology was appropriate for Al-rich sewage sludge ashes, which achieved around 78% efficiency of P-recovery. Kalmykova and Karlfeldt Fedje (2013) tested two chemical approaches for P recovery from municipal solid waste incineration fly ash. Besides the low initial concentration of P, they found that high concentration of calcium (Ca) and other metals was the major obstacle that hinder an effective P recovery.

Sulphuric acid is one of the most efficient extractants of phosphorus (Fang et al., 2018). Cohen (2009) determined the amounts of H_2SO_4 required for P dissolution from incinerated sewage sludge and animal carcasses. The researcher illustrated that about 85% and 73% of P could be obtained from sewage sludge and animal carcasses ashes, respectively, for which 0.78 and 0.69 kg H_2SO_4/kg ash were the optimum acid amounts, respectively. To our best knowledge, few works have investigated P recovery from animals' wastes; they mostly focus on animals' manures (Sampat et al., 2018; Sarvajayakesavalu et al., 2018). Meanwhile, almost no study have focused on P recovery from fish bones using chemical approach, although fish bones contain high P concentration (Sontang Sihotang et al., 2019).

Fundamentally, bones of humans and animals are composed of two main elements: Ca and P. Generally, animals' waste bones are a major sink for phosphate compounds. Nevertheless, animals' waste bones were rarely considered for P recovery applications. In Malaysia, fish meals are very common food, which produce huge amounts of waste containing considerable rates of P. On other hand, only 3 to 7% of P (P-solid wastes and P-wastewater) in Malaysia is recycled back into the environment (Ghani and Mahmood, 2011). Therefore, it is essential to investigate alternative P sources to be able to cover the growing demand of P.

The main objectives of this study is to characterize the fish waste bones ash (FWBA), and to determine the optimum condition of recovering P from the ash using H_2SO_4. Theoretically, sulphuric acid reacts with calcium-phosphate compounds according to the following equation:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4\downarrow \quad (1)$$

Following this approach, P can be selectively separated from Ca, and dissolved as reactive phosphate (HPO_4^{2-}), which makes the recovered P-rich solution more beneficial for specific applications such as struvite precipitation (Farrow et al., 2017).

Materials and Methods

Preparation of the Ash Samples

Samples of fish waste bones were collected from a restaurant that serves different fish species including Tilapia (*Oreochromis niloticus*), Grouper (*Epinephelus*) and Cod (*Gadus*). After removing the left-over meats, the waste bones were incinerated twice at 600 °C for 2 h at each turn, using a muffle furnace (Carbolite, 1990), in order to have a complete combustion for the organic content.

Characterization of Fish Waste Bones Ash

The structure of the FWBA was analyzed by X-ray diffraction test (XRD, Siemens D5000, Geramny). Step-scanning was applied with 2θ step intervals of 0.05° from 20° < 2θ < 60° and a stepping time of 1 s/step. The elemental composition of the ash was determined by dissolving 0.1 g of FWBA using closed-digestion method (aqua regia). A mixture of hydrochloric acid (HCl, 37%) and nitric acid (HNO_3, 67%) with a volume ratio of 3:1 was applied to implement the digestion. Measurement of Ca, K, Mg and Fe was carried out by atomic adsorption spectroscopy (AAS, 3300, Perkin Elmer, USA), and Inductively Coupled Plazma-Mass Spectroscopy (ICP-MS: OPTIMA 7300 DV, PerkinElmer, USA) was used to analyse As, Al, Cd, Cr, Cu, Ni and Zn.

Phosphorus Extraction Experiments

Through two consecutive stages, three factors were studied: acid concentration (molarity), acid amount and dissolution time. In the first stage, samples of 1 g of FWBA were mixed with different amounts and concentrations of sulphuric acid and shaken for 2 h, as indicated in Table 1. The samples were shaken at

Table 1: Acid/Ash ratio and concentrations tested for P extraction

Amounts of applied acid* ($kg\ H_2SO_4/kg$ ash)	Acid/Ash ratio (mL/g ash)			
	1.0 M H_2SO_4	1.5 M H_2SO_4	2.0 M H_2SO_4	3.0 M H_2SO_4
0.4	4.1	3.0	3.8	-
0.6	6.2	4.2	3.2	3.0
1	8.2	7.0	5.2	3.5
1.5	15.3	10.3	7.7	5.2
2	21.0	14.0	10.4	7.0

* H_2SO_4 is expressed as 100%.

room temperature, using an orbital shaker (Hotech, Model 721) operated at a speed of 120 rpm. At the end of the reaction time, aqueous samples were recovered using 0.2 μm nylon syringe filters (Whatman, UK) and analysed colorimetrically for reactive P (PO_4-P) concentration with a spectrophotometer (Hach DR 6000, USA), according to APHA Standard Methods (APHA, 2005). In the second stage, the optimum condition obtained in the first stage was applied at different periods of time, to investigate the effect of time on P extraction. All experiments were duplicated.

Results and Discussion

Characteristics of Fish Waste Bones Ash

XRD analysis was applied to characterize the structure of FWBA powder. The X-ray diffractogram exhibited several peaks that indicated the presence of apatite compounds as illustrated in Figure 1. The XRD pattern generated from the FWBA matched well with carbonate-apatite ($Ca_5(PO_4)_3CO_3$) database model, i.e. position and intensity of the peaks, which was probably the major compound.

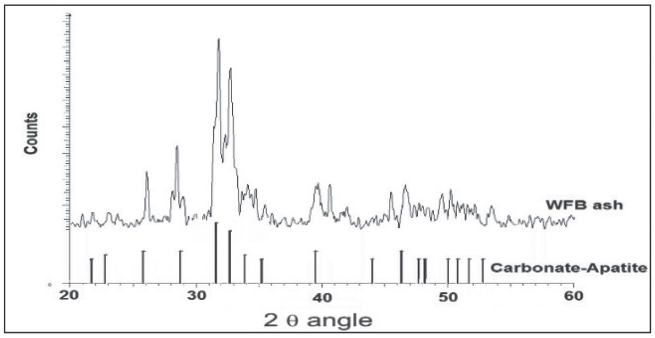

Figure 1: The XRD analysis of FWBA powder.

The result of the chemical composition analysis of the FWBA, shown in Table 2, indicates that Ca and P are the predominant elements in the ash, which represented about 22.7% and 16.9% by weight, respectively. Coutand et al. (2008) and Deydier et al. (2005) reported similar values of P content for meat and bone meal (MBM) ash (16.2 and 18.37 wt.%, respectively). Moreover, the Ca/P ratio for the FWBA is around 1.34, which is between the ratio for sewage sludge ash (1.24) and animal carcass ash (1.66). Potassium (K), magnesium (Mg) and iron (Fe) accounted for about 2.47 wt.%, while

Table 2: Composition of actual landfill leachate

Element	Fish waste bones ash (this study)	Animal carcass ash (Cohen, 2009)	MSW fly ash (Kalmykova and Karlfeldt Fedje, 2013)	Sewage sludge ash (Petzet et al., 2012)
Ca	227	305	141	98
P	169	183.4	5.9	79
K	18.6	12	54	12
Mg	4.8	6	13	12
Fe	1.3	7	19	38
Zn	0.186	-	37	3.81
Al	0.096	5	23	45
As	0.081	-	0.46	-
Cu	0.009	-	2	0.84
Cr	0.006	-	0.49	0.25
Ni	0.003	-	0.1	0.095
Cd	0.002	-	0.27	0.005

heavy metals content was less than 0.038 wt.%. These percentages were very low compared to other kinds of ash, especially those generated from incineration processes of municipal solid waste (MSW) (Kalmykova and Karlfeldt Fedje, 2013) and sewage sludge ash (Ito et al., 2013). These characteristics support the recovery of P from FWBA, as the major obstacle is only the high concentration of Ca. Therefore, using H_2SO_4 as a separation media could be more viable (Equ. 1).

Extraction of Phosphorus

The dissolution of P increased significantly with increasing the concentration of H_2SO_4 from 1 M to 2 M. However, the efficiency of P extraction decreased considerably when 3 M H_2SO_4 was applied. This reduction could be referred to the rapid reaction dissolution of other compounds instead of P compounds. Figure 2 presents the effect of the applied amount of H_2SO_4. It illustrates that P extraction could be increased by increasing the amount of acid; however, the extraction rate decreased after reaching an optimum value. The best results of P dissolution were obtained in the range of 1-1.5 kg acid/kg ash for all tested molarities, except for 3 M. It was found that more than 97% of P content could be released when 2 M H_2SO_4 was applied with the ratio of 1.5 kg acid/kg ash. Cohen (2009) reported that the amount of H_2SO_4 required to extract 73% of P from animal carcass ash using 1 M H_2SO_4 was around 0.69 kg H_2SO_4/kg ash. However, in terms of P recovery efficacy, the current study shows that more than 77% of P extraction can be achieved if the same acid amount and concentration was applied (Figure 2), although the original P content of the FWBA is quite lower than the animal carcass ash (Table 2).

Table 3 illustrates a comparison between the results obtained in the current study and Cohen (2009) who used sulphuric acid to recover P from different kinds of ash. H_2SO_4 required to recover P from FWBA is higher than required for carcasses ash and lower than required for sewage sludge ash. The reason behind that could be likely the difference in the original P content of these ashes, i.e., the lower initial P, the higher sulphuric acid consumption. Additionally, the comparison in Table 3 shows that the FWBA is competent with other types of ash as an alternative P source, even though the acid consumption is quite high. Further, more research is required to develop this approach and make it more feasible and sustainable.

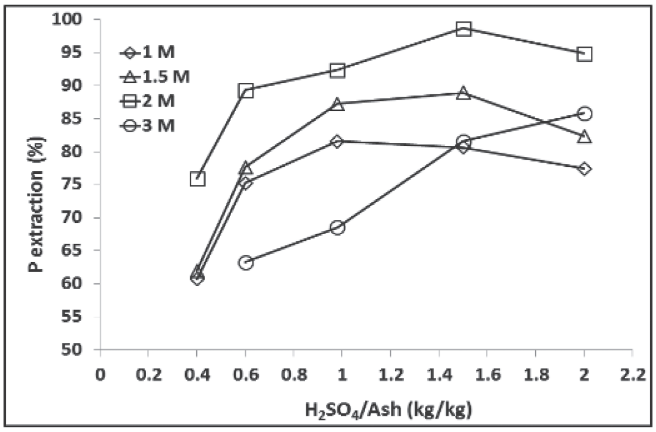

Figure 2: Phosphorus extraction from FWBA at different acid/ash ratios.

Applying the acid with a ratio larger than 1.5 kg H_2SO_4/kg ash has resulted with a slight drop in the P extraction efficiency. This could be, however, due to the rapid formation of gypsum ($CaSO_4.2H_2O$) around ash aggregates, which might have prevented the acid from reacting with all ash particles, so reduced P extraction.

Effect of Time

Applying the optimum P dissolution condition, the efficiency of P extraction was tested at different periods of time. As demonstrated in Figure 3, extraction of P increased rapidly during the first 60 min. After 90 min, the dissolution reaction became almost stable, in which there was no significant increase in P extraction efficiency. This result is consistent with other studies that tested chemical dissolution of P from different kinds of ashes, which showed that 2 h was enough to complete the reaction (Kalmykova and Karlfeldt Fedje, 2013; Cohen, 2009).

Table 3: Comparison of H_2SO_4 consumption between Cohen (2009) and the current study

	Current study	*Cohen (2009)*	
	FWBA	*Animal carcasses*	*Sewage sludge*
Original P content (wt. %)	17.00	18.34	6.20
P-dissolved (g/kg ash)	166.6	131.4	66.6
Acid consumption (kg H_2SO_4/kg P-dissolved)	8.8	5.2	10.5

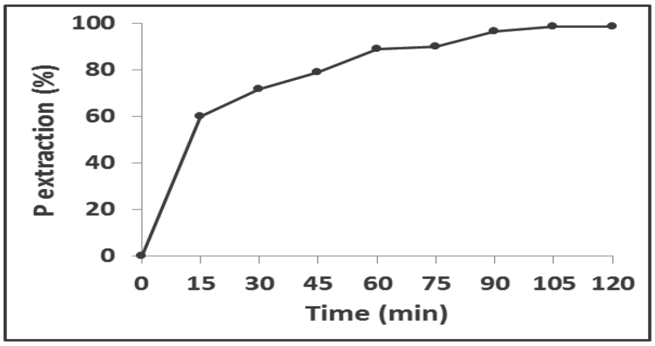

Figure 3: Effect of time on P extraction (2 M H_2SO_4, 1.5 kg H_2SO_4/kg ash).

Conclusions

Phosphorus recovery from waste materials gains a global concern, as the conventional P sources (rock apatites) are neither sustainable nor renewable; they could be completely depleted within the coming 50-100 years. Food wastes are considered as one of the P sinks, however not utilized efficiently. The current study focused on P extraction from FWBA using sulphuric acid. The ash characterization reveals that it contains reasonable amount of P (17 wt.%). The experimental work proves that P recovery is significantly influenced by acid amount and concentration. Around 97% of P contained in the ash could be recovered in the form of rich P solution using 2 M H_2SO_4 and 1.5 kg acid/kg ash. In addition, it was shown that the dissolution reaction could be completed during a short period of time, which was less than 2 h. In future, further studies should be carried out to investigate P recovery from other types of wastes using different chemical approaches, in order to maintain alternative P sources that could replace the conventional ones.

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