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Technique of Phosphorus Recovery from Charcoal of the Water Sludge by Hot Alkali Water Extraction

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ABSTRACT

In order to make utilize the charcoal of water sludge, charcoal of the sludge was mixed with a aq. solution of NaOH or KOH, and heated at 90°C - 120°C. Phosphorus was extracted by the addition of hot water, and separated by filtration. The phosphorus in the filtrate was recovered through crystallization followed by concentration and cooling at a low temperature. The recovered phosphorus was considered sodium phosphate (Na_3PO_4 $12H_2O$) or potassium phosphate (K_3PO_4 H_2O) from the recovered condition and X-ray analysis. The phosphorus recovery rate was estimated at about 60%-70% Reuse of the alkali which was not used in the recovery process, and the concentration method of the extracted phosphorus was investigated.

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Introduction

A large amount of wastewater sludge is discharged through the construction of sewage treatment facilities, and a recycles or reduction of them is an important matter [1]. The water sludge contains a significant amount of phosphorus, and the phosphorus concentration in the sludge is increased by the introduction of the advanced phosphorus removal technique [2]. However, a practical recycling technique is not established, and some are used as a compost for fertilizer, but this usage is not popular because of the hygienic factor [3]. In Japan, most of the sludge is now incinerated through heat energy recovery to reduce the amount of the waste.

To solve the problem, one method, carbonization, has been introduced, and some carbonization plants are constructed in Japan [4]. This charcoal is regarded as useful for many usages, as a fuel, reducing agent or absorbent, however, the carbonized sewage sludge contains higher ash content compared to ordinary wood-based biomass ash, and the utilization of the charcoal is limited [5].

In order to expand the utilization of the charcoal, the phosphorus recovery techniques are regarded as useful, and some studies of chemical extraction methods using acid or alkali are has been investigated [6,7].

The phosphorus is considered to exist mainly as a form of aluminum phosphate in the sludge. We found that phosphorus in the charcoal or ash can be effectively extracted under hydrothermal conditions compared with a conventional alkali extraction method, and we investigated the practical phosphorus recovery conditions [8].

Basic Procedure of the Phosphorus Recovery

The raw charcoal is mixed with the aq. solution of alkali metal hydroxide (NaOH or KOH), and heated at 90°C to 120°C. Later, the phosphorus in the charcoal is extracted by addition of the hot water. The extracts are concentrated to enough concentration to make a crystal of the phosphate compounds, and recovered by the crystallization with residue water (Figure 1).

Condition for the Phosphorus Recovery

In order to find out the best conditions for the phosphorus recovery, some investigations were carried out using the Charcoal A and B. The charcoal which was made by carbonization in an anaerobic chamber at 700°C was used. The chemical compositions of the ash components of the charcoal are shown in Table 1.

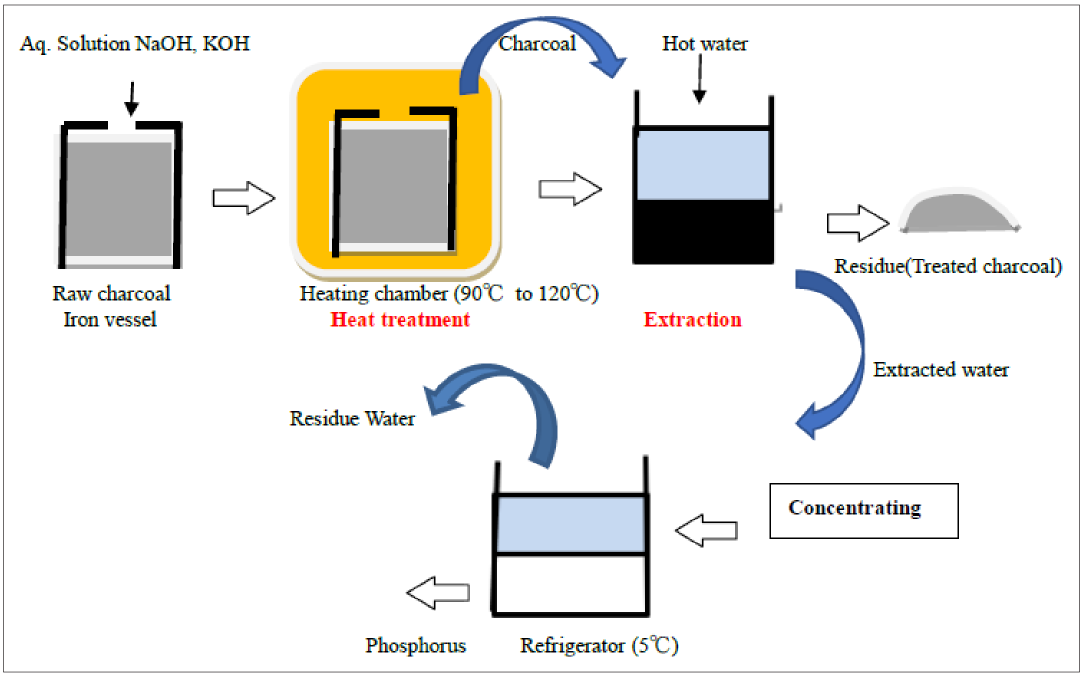

Figure 1: Basic Phosphorus recovering procedure

Temperature

50g of the Charcoal A was mixed with aq. solution of NaOH (30g with 50mL of water), and put into the small iron vessel (capacity; 300mL). In order to maintain atmospheric pressure, a small hole is made on the top of the vessel. The vessel was stored in the heat chamber, and the chamber was maintained at some temperature (room temperature to 135 °C) for 2 hours. Later the treated mixture was transferred into the iron vessel (volume; 1000ml) which was heated about 90 °C, and phosphorus was extracted by the addition of the water (about 500mL) followed by the solid-liquid separation. The phosphorus concentration of the filtrate was analyzed by chemical color metric analysis.

The amounts of the phosphorus extracted from the charcoal increased with the temperature of the heating chamber towards room temperature to 100 °C, and tend to be flat around to 100°C to 135°C. The trend of the temperature dependances are the same as the previous research which was carried out with pressurized conditions [9].

Table 1: Chemical composition of the ash of the charcoal used in this experiment

	carbon	SiO_2	Al_2O_3	CaO	P_2O_5	MgO	Fe_2O_3	Na_2O	K_2O	Other
Charcoal A	58.2	15.5	12.7	10.8	39.8	2.2	11.1	0.2	3.9	3.8
Charcoal B	37.7	27.5	23.1	6.1	21.8	3.1	11.4	2.7	1.8	2.5

Table 2: Optimal recovery condition

Solid liquid Mixing rate for the heat treatment	Charcoal 50g aq. Alkali solution 70mL
Alkali addition rate	NaOH or KOH 6g in 10g of charcoal
Temperature of the heating chamber	120 °C
Heating time	2 hours

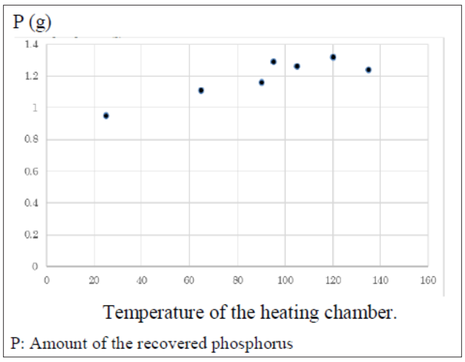

Figure 2: Temperature dependance of the phosphorus recovery

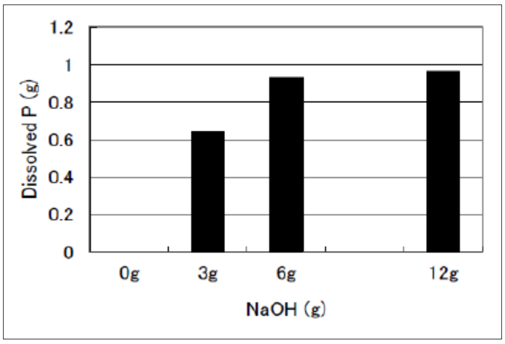

Figure 3: NaOH addition rate

Solid -Liquid Mixing Rate

In order to find out the optimal mixing rate (liquid and solid) of the charcoal and aq. alkali solution, 50g of the Charcoal A was mixed with 50mL to 500mL of the aq. solution of NaOH (total amount of NaOH is same: 30g), and treated at 120 °C) as mentioned way. From the result, the mixing ratios; charcoal 50g and aq. solution 50mL to 70m are considered to be better.

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Almost the same trends are found on the phosphorus recovery using KOH, and the phosphorus recovery condition was decided as shown in Table 2.

Result

Phosphorus Recovery Rate and Feature of the Recovered Phosphorus

50g of the charcoal was mixed with an aq. solution of NaOH or KOH, and treated as described. The treated charcoal was incinerated for the analysis, and the chemical components of the ashes were analyzed using Xray analyzer (BRUKER, S2RANGER).

The phosphorus recovery rate was calculated as follows

P (%) = (P1×A1 – P2×A2) ÷ P1×A1×100

Ash content of the non-treated charcoal: A1(%)

Ash content of the treated charcoal: A2(%)

Phosphorus content of the non-treated charcoal: P1 (phosphorus g / g ash)

Phosphorus content of the treated charcoal: P2 (phosphorus g / g ash

The phosphorus recovery rate was estimated to be 58% to 71% (charcoal A and charcoal B) in this experiment as shown in Table 3. Phosphorus recovery rate was estimated to be 76% to 77%, which is higher compared to the result which was carried out using NaOH [10].

Table 3: Phosphorus recovering rate

	NaOH	KOH
Charcoal A	58%-68%	
Charcoal A		76%-77%
Charcoal B	68%-71%	

The Feature of the Recovered Materials

50g of the charcoal was mixed with aq. solution of NaOH (NaOH: 30g with water: 70mL), and treated as described. Later the phosphorus containing filtrate (500mL) was concentrated to 150mL (which can make crystalized phosphorus salts), and cooled at 5°C one night, and recovered as crystal with 70mL of the residue water, The residue water contained significant amounts of alkali (estimated 10g NaOH by the acid-alkali titration analysis).

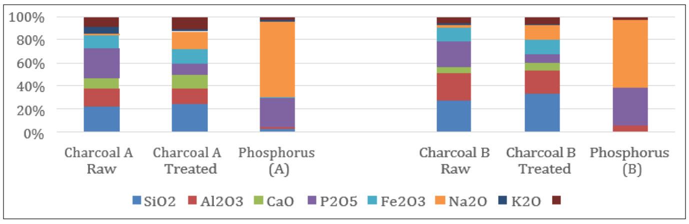

Figure 4: Chemical composition of the recovered materials

The ash components of the treated charcoal were mainly composed of SiO_2, Al_2O_3 and Na_2O as shown in the Fig.4. The amount of the phosphorus was degreased by the extraction, however, not a significant amount of the non-reacted P_2O_5 remained in the charcoal. The components of CaO, Fe_2O_3 in the charcoal were relatively increased by the treatment because of the elution of the phosphorus. On the contrary, Na_2O content was increased by the treatment, as a result of the reaction of NaOH and the ash components in the charcoal.

The recovered phosphorus is mainly composed of Na_2O and P_2O_5, and a small amount of Al_2O_3. Recovered phosphorus is considered mainly composed of sodium phosphate (Na_3PO_4 $12H_2O$) from the chemical composition and the recovered condition (pH>13), and Xray diffraction analysis are shown in Figure 5.

The phosphorus which is recovered by KOH, is considered to be a form of K_3PO_4 which is very hygroscopic, therefore direct dehydration is difficult. In order to solve the matter, neutralization was hygroscopic, and carried out using HCl.

The phosphorus recovered by KOH was mainly composed of K_2O and P_2O_5 and KCl, and considered to be KH_2PO_4 by chemical composition and X-ray diffraction analysis.

The appearance of the treated charcoal is black grain, and the ash components and gravity were degreased by the treatments (Table 4), and this will be an advantage for the utilization of the treated charcoal.

Table 4: Feature of the charcoal

	Color and	Specific gravity	Ash contents (%)
Charcoal A	Black particle	---	62.3
Charcoal A(treated)	Black particle	---	56.2
Charcoal B	Black particle	0.41	43.8
Charcoal B(treated)	Black particle	0.38	38.7

Additional Investigation Reuse of the Alkali Residue Water

A significant amount of alkali remained in the residue water, and the reuse of the alkali is considered to be very important. In this experiment, about 70mL of the residue water was discharged from phosphorus recovery (50g of charcoal), and the residue water contains almost 10g of alkali components (as a form of NaOH) as described.

In order to confirm the reuse of the alkali, as 1st Run, 30g of NaOH was mixed with 50g of charcoal, and phosphorus recovery was carried out as described above. As 2nd Run, 20g of NaOH was mixed with the residue water of the 1st Run, and treated the same way. As 3rd Run 20g of NaOH was mixed with the residue water of the 2nd Run, and treated the same way [11]. The amounts of the recovered phosphorus were almost the same in 1st run as the 3rd Run, and reuse is considered to be possible.

This experiment was repeated the same way (experiment A and experiment B) as is shown in the Figure 8.

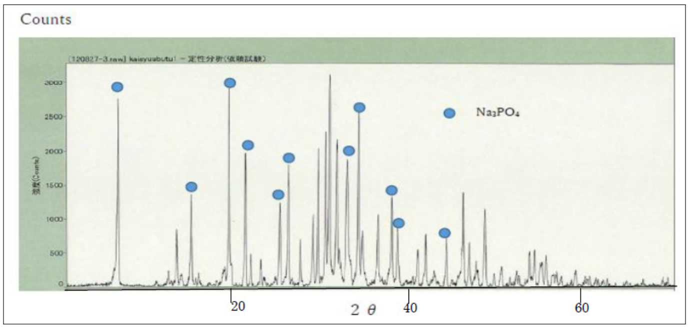

Figure 5: XRD of the recovered phosphorus using NaOH

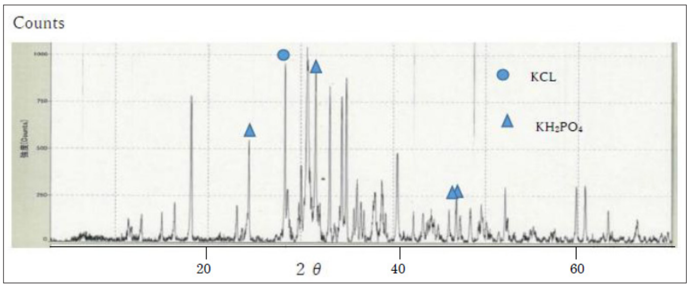

Figure 6: XRD of the recovered phosphorus using KOH

Phosphorus Containing Filtrates Concentrating Method

The phosphorus containing extract has to be concentrates to enough density which can crystallize alkali phosphate. In order to concentrate the extracts, usually, evaporation techniques are used. However, evaporation consumes much energy. The extraction method with a low liquid-solid ratio is regarded effective in this regard. However, in a low liquid-solid ratio, significant amounts of the phosphorus will remain in the filter mass. To solve the matter, multistage filtration was investigated. Experiments are as follows.

In the 1st run, 50g of the charcoal, was put into the reactor vessel and mixed with 70ml NaOH aq. solution and phosphorus recovery was carried out as described. After the heat treatment, the charcoal was transferred into the vessel, mixed with 150mL (Solid/liquid:1:3) of water, and extraction was carried out, which recovered about 150mL of filtrates (Extract (1)). The extract (1) was cooled in the refrigerator, and phosphorus was recovered. The significant amount of the phosphorus remained in the filter mass. In order to extract the remaining phosphorus, 150mL of washing water was added to the filter mass, and 150ml of the Extract (2) was discharged. Extract (2) was added to the extraction for the 2nd Run. These extractions were repeated as shown in the Figure 9.

Repeating the treatments (1st Run to 4th Run), the phosphorus concentrations in the filtrate (1) are increased to the density which can recover the phosphorus without concentrating treatments (evaporation technique) as shown in the Figure 10 [12].

This experiment was repeated the same way (Experiment A and Experiment B)

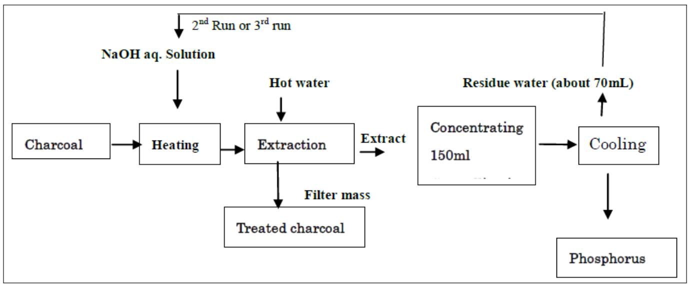

Figure 7: Experimental method for the reuse of the residue alkali water

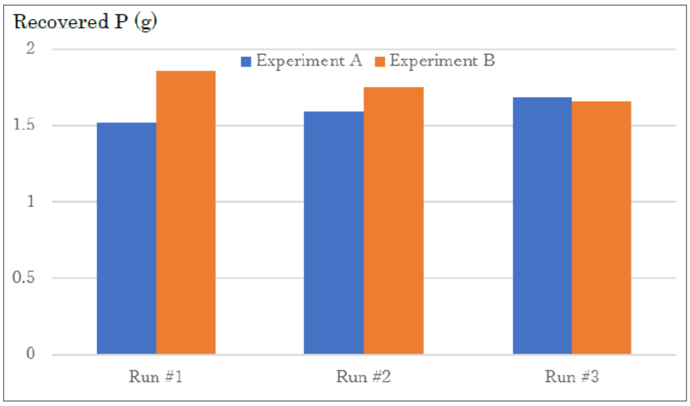

Figure 8: Reuse of the residue alkali water

Future Prospect for the Method

Recovered Phosphorus

The recovery rate of the phosphorus reached from 58% to 71 % using NaOH, and 76%-77% using KOH. The recovered phosphorus was considered to be alkali metal phosphate (considered to be sodium phosphate or potassium phosphate) which have many usages and also can be refined using crystallization techniques.

In this experiment, heat treatments were carried out at 120°C, but the treating temperature considered to be enough around 100°C, and operated at atmospheric pressure, the treatment is considered to be an easy way.

Adaptability Against Various Kinds of the Raw Charcoals

The chemical composition of the ash components of the charcoal differs depending on the discharging source. The phosphorus recovery of this method is considered to be caused by the reaction between alkali metals and silicon and aluminum in the ash components [13]. Therefore, the composition of those components is regarded to have a large effect on the recovery rate. The recovery rate is considered to depend on from where the raw charcoals originated, and some adjustment of the method will be needed depending on the raw charcoals.

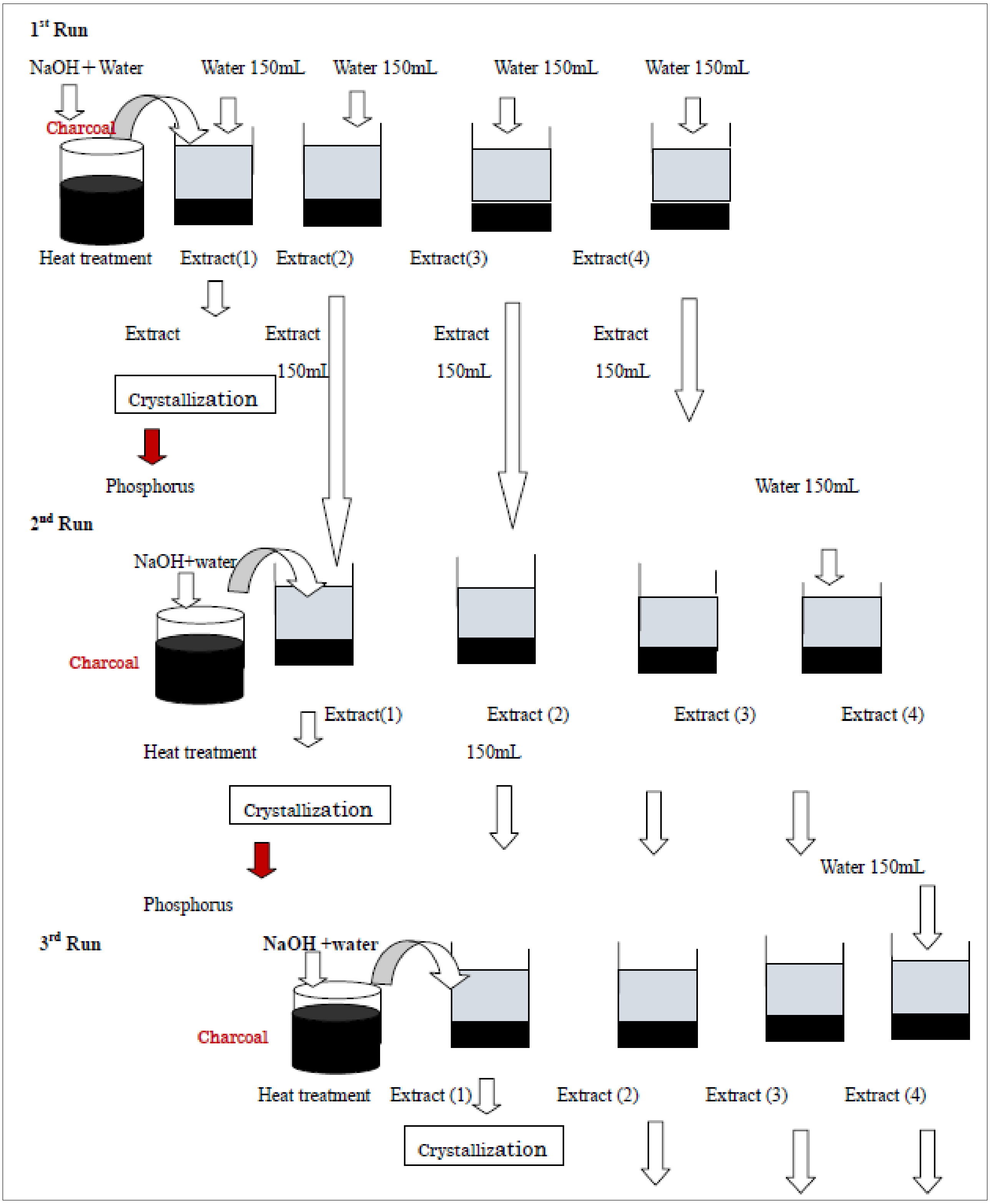

Figure 9: Multistage filtration method

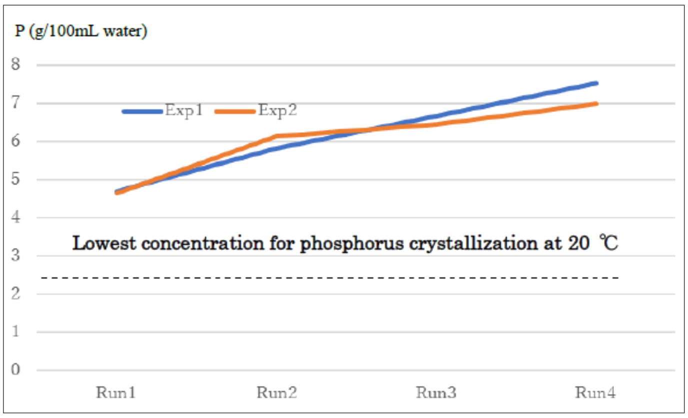

Figure 10: Phosphorus concentration in the extract (1)

Usage of the Treated Charcoal

The phosphorus removed charcoal has less ash components, and can be widely used for many usages like fuel, agriculture etc., and many carbonization plants will be constructed in future.

Phosphorus recovery from the charcoal is a simple and energy effective process, and considered to be useful. However, many more carbonization plants should be constructed, and the practical technique needs to be developed,

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