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Phosphorus Recovery from Sewage Sludge via Pyrolysis

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1. Introduction

The Brundtland Report (WCED, 1987) draws attention to the rapidly depleting the Earth's resources, particularly food and energy. In case of energy, there are two major problems. First, the rapid depletion of non-renewable natural resources. Second, global climate change caused by excessive emission of carbon dioxide (Pawłowski, 2009; Udo i in., 2011; Duran i in, 2013).The intensification of negative changes favor the socio-political system which is liberal capitalism (Pawłowski, 2012).

Availability of phosphorus (P) sources has been largely ignored in research and policy debates. In recent years, the supply of phosphorus resources has become a concern because the raw material in phosphate reserves is being depleted around the world (Abelson, 1999; Vaccari, 2009). Phosphorus is an essential element for food production and nearly 90% of mined phosphate rock is used for production fertilizers. There is no substitute for phosphorus in the food supply (Cordell, 2009). However, it can be recovered and reuse from different waste streams. One of the sources of this raw material may be sewage sludge (Montusiewicz i in., 2008; Pawłowski, 2008) Sludge pyrolysis is an innovative process that can convert both raw and digested sludge into useful bioenergy (oil and gas) and biochar (Cao and Pawłowski, 2012a; 2012b).

The aim of this study is to determine the amount of phosphorus that can be recovered through pyrolysis of sewage sludge generated in the Lublin province.

2. Global phosphorus scarcity

Phosphorus (P) is an essential element for all living organism that cannot be substituted. More than 90% of the mined P is used for agricultural purposes, mostly for the P fertilizers (Cordell et. al, 2009; Dery and Anderson, 2009). The increase in world population, as well as the cultivation of energy crops significantly contributed to the decrease of the phosphate rock reserves (Matsubae et. al, 2011). It is predicted that P demand will increase from 1,5 to 3,6% each year (Cordell and White, 2011). Estimates are that the resource could be exhausted in 100–250 years (Steen, 1998; Smil, 2000). Furthermore, Cordell et al. (2009) predict phosphorus peak in 2033, after this moment production will decline. Another issue is that the global production of agricultural products depends on a small number of countries, mainly Morocco, Iraq and China.

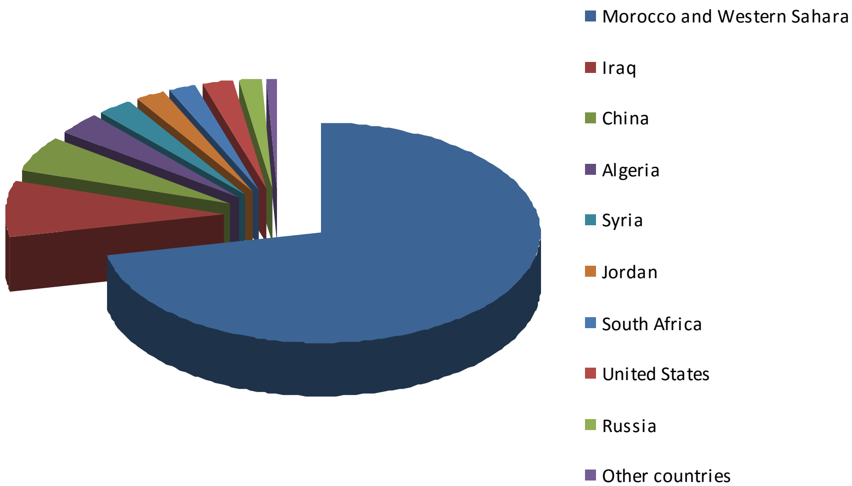

Fig. 1. Global phosphate rock reserves (USGS, 2012)
Rys. 1. Światowe zasoby fosforytów (USGS, 2012)

Approximately 191 Mt of phosphate rock were mined in the world in 2011 (USGS, 2012). Of this, 72 Mt was explored in China, – 28,4 Mt in the USA, and 27 Mt in Morocco. Moreover, there are no essential deposits of phosphate in the EU. At the moment extraction of those reserves are not possible for economic and technical reasons.

3. Phosphorus recovery

Currently, several innovative phosphorus recovery technologies have been proposed (Hermann, 2009; Mavinic et al., 2009). Generally, phosphorus recovery is possible from the liquid phase such a side streams, as well as from the sewage sludge and the sludge ash. In the literature, two main categories of P-recovery technologies have been presented: wet chemical approaches and thermochemical approaches. Thermochemical technology separate P and heavy metals at temperatures of 1000–2000°C and transform P into a plant-available form. Whereas, in wet chemical technology sewage sludge is dissolved by adding acid or base, in combination with temperature. After the insoluble compounds have been removed, phosphates could be separated from the phosphorus-rich liquid phase by precipitation, ion exchange, nanofiltration (Cornel and Schaum, 2009). The comparison of available P – recovery technologies is shown in Table 1.

Nowadays, there is limited experience in industrial-scale implementation. Thus the total cost of phosphorus recovery technologies is difficult. According to Balmer (2003) the cost of phosphorus recovery from sewage sludge was estimated about €8,800/(Mg·P). Whereas, the price of phosphate rock from Morocco was €127/(Mg·P) (February 2013). Presently, the total expense for recovered phosphate exceed the costs for phosphate from rock phosphate by several times.

3.1. Pyrolysis

Thermal process such a pyrolysis has usually been applied for energy recovery. Additionally, recovery of phosphorus could be achieved via this method.

Pyrolysis is a process to convert biomass directly into solid, liquid and gaseous products by thermal decomposition in absence of oxygen (Vamvuka, 2011). The gas fraction contains carbon dioxide, carbon monoxide, methane, hydrogen, ethane, ethylene and other compounds, the calorific value of this phase ranges from 15 to 30MJ/Nm^3. The liquid phase encloses water (15–35%) and organic chemicals, such as acids, alcohols, aldehydes, ketones, esters, phenols and nitrogen compounds The solid fraction, also known as a biochar contains mostly ashes, inert substances and heavy metals (Bień, 2007). The proportion of these phases depends on the operational conditions of the process, such a temperature, pressure and retention time, as well as type of the feedstock (Werle and Wilk, 2009).

Table 1. Examples of phosphorus recovery systems (Bridle and Pritchard, 2004; Cornel and Schaum, 2009; Cordell et al., 2011)
Tabela 1. Przykłady systemów odzyskiwania fosforu (Bridle and Pritchard, 2004; Cornel and Schaum, 2009; Cordell et al., 2011)

process	input	output	recovery rate	characteristic
OSTARA	mixed wastewater	Crystal Green struvite (5–28–0 + 10% Mg) slow release fertilizer	> 85 %	fluidized-bed reactor, requires constant addition of Mg, effluent waste stream still needs treatment and proper disposal (contains heavy metal)
CRYSTA-LACTOR®	wastewater	high purity phosphate crystal pellets	70–80 %	cylindrical fluidized-bed reactor with sand as seed material
SEPHOS	sewage sludge ash	aluminium phosphate	90 %	the elution of the sewage sludge ash with sulphuric acid, removing undissolved residuals, the pH-value in the filtrate is increased stepwise, at pH 3.5 aluminium phosphates precipitate
ENER-SLUDGE	sewage sludge	char	100 %	pyrolysis of dry sludge at 450°C and a pressure 1–5 kPa in the absence of oxygen

Pyrolysis could be classified as slow and fast. Slow pyrolysis is characterized by slow heating rate and long residence time. This type of pyrolysis has usually been used for the production of biochar, which could be used as a soil amendment. Fast pyrolysis involves rapid heating rates (around 100°C/min) (Cao and Pawłowski, 2012a, b). It has mostly been applied to produce gas and liquid fractions, which allows recovery of energy. Furthermore, pyrolysis can be carried out in two temperature ranges: 470–700°C (low-temperature pyrolysis) and 900-1100°C (high-temperature pyrolysis) (Bień 2007; Piecuch et al., 2011; Vamvuka, 2011). Pyrolysis presents certain advantages over the other methods of sewage sludge utilization. The volume of solid residue is significantly reduced. Moreover, the heavy metals present in the solid phase are relatively resistant to natural lixiviation. The liquid and gas phase could be used as potential fuels. The liquid phase could be easily stored and transported, may also be used as a substrate in a petrochemical industry. Additionally, phosphorus and heavy metals could be recovered from the solid fraction. In comparison with other methods of thermal utilization of sewage sludge pyrolysis is characterized by low gas emission (Piecuch, 2000).

4. Materials and methods

Sewage sludge for an analysis was obtained from two municipal mechanical-biological wastewater treatment plants located in Lublin Province (WWTPs Lublin and Puławy). The average capacity of WWTP in Puławy is 13 500 m^3/d. In this plant, sewage sludge disposal system consists following major unit process: thickening, anaerobic sludge digestion, dewatering. The second of them, MWWTP in Lublin has a capacity of 65 000 m^3/d. The sewage sludge disposal system includes additionally heat drying (fluidized-bed dryer). For the experiments the following types of sludge have been sampled:

- raw sludge – mixed at a volume ratio of 60:40 (primary:waste sludge),
- dewatered sludge – from filter presses,
- dried sludge – sampled only from WWTP Lublin from fluidized-bed dryer.

The analyses of total phosphorus were performed with ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). Dry mass content, was determined according to PN-EN 12880 standard. The presented results are the average of three replicates.

According to the Central Statistical Office, in 2011 in Poland produced over 519,2 thousand tons dry masses of municipal sewage sludge. However, in Lublin Province worked 268 MWWTP with a total capacity of 350,005 m^3/d, which generated 21,8 thousand tons dry masses of municipal sewage sludge.

In studies conducted by Bridle and Pritchard (2004) and Wang et al. (2012) full recovery of P from sewage sludge after pyrolysis at 450°C was achieved.

5. Results and discussion

The results of the study are shown in Table 1 (average data are reported). Analyzed sewage sludge was characterized by a low content of phosphorus, from 0,24 to 0,77% P of dry matter (DM). According to EU report *Disposal and recycling routes for sewage sludge* total phosphorus concentration in sewage sludge produced in European MWWTPs was between 0,9 to 5,2% of DM (2001).

Table 2. Content of phosphorus in different types of sewage sludge, % P of DM
Tabela 2. Zawartość fosforu w różnych typach osadów ściekowych, % P w sm

types of sludge	MWWTP	
	Lublin	Puławy
raw	0.26	0.29
dewatered	0.24	0.26
dried	0.77	–

The concentration of phosphorus in raw and digested sludge was lower than in studies conducted by Bień (2007) (Table 2). Moreover, total phosphorus content in the raw sewage (mixture of primary and waste sludge) was lower than in the case of dewatered sludge, which could be due to the release of phosphorus into liquid phase.

There are no essential differences between total phosphorus concentration of sewage sludge samples from the MWWTP in Lublin and sludge from MWWTP in Puławy.

Table 3. Content of phosphorus in different types of sewage sludge, % P of DM (Bień, 2007)
Tabela 2. Zawartość fosforu w różnych typach osadów ściekowych, % P w sm (Bień, 2007)

types of sludge	P_t
raw (primary)	0.4–3.0
raw (waste)	0.0–1.5
digested sludge	0.3–0.8

It has been observed that both raw and digested sludge can be used for pyrolisis. However, preferred solution is a two-stage process (the combination of anaerobic digestion and pyrolysis) by Cao and Pawłowski (2012).

Estimated that as a result of pyrolysis of dried sludge can be recovered approximately 1670t of phosphorus per year in the Lublin province. This is relatively small amount, but with recovered energy allowed to maximize the potential of sewage sludge.

6. Conclusions

Accessibility of phosphorus sources is critical to our future. It is one of the most abundant element in the earth's crust. However, its deposits are geographically located only in a few countries; mainly in Morocco, Western Sahara and Iraq. The uneven distribution of one of the world's most important resources presents significant risk of potential conflicts. Furthermore, the European Union is dependent on import of this raw material. In the literature several innovative phosphorus recovery technologies was described, however this practice is not common. Pyrolysis of sewage sludge is not a new solution. So far, this method has mainly been used for energy recovery. In recent years, more attention has been paid to the possibility of recovery phosphorus and heavy metals present in the solid phase. Moreover, in comparison with other technologies, pyrolysis of sewage sludge has a very high recovery rate (approximately 100%).

In this study, it was estimated that as a result of pyrolysis of dried sludge can be recovered approximately 1670t of phosphorus per year in the Lublin province. The concentration of phosphorus in sludge samples was in the range of 0,24 to 0,77% P of dry matter and it was significantly lower than the level of this compound given in literature.

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Odzysk fosforu z osadów ściekowych z wykorzystaniem procesu pirolizy

Streszczenie

Wyczerpywanie się złóż fosforytów, stanowi obecnie jeden z najpoważniejszych światowych problemów, który może doprowadzić do kryzysu produkcji żywności. Blisko 90% światowego wydobycia tego surowca stanowi surowiec do produkcji nawozów. Szacuje się, że przy obecnym poziomie zużycia tych złóż w ciągu 50–100 lat ulegną one wyczerpaniu. Natomiast już w 2033 nastąpi tzw. szczyt wydobycia fosforu – *Peak phosphorus*. Po osiągnięciu tego momentu światowe wydobycie będzie już tylko malało, aż do chwili całkowitego wyczerpania złóż.

W związku ze wzrastającą liczbą ludności, zapotrzebowanie na fosforyty będzie stale rosło. Zasoby tych złóż są nieodnawialne, dlatego też pojawia się konieczność odzysku tego pierwiastka. W chwili obecnej recykling i ponowne wykorzystanie fosforu nie jest praktyką powszechnie stosowaną, pomimo wielu badań opisujących te zagadnienie. Obecna sytuacja wymaga podjęcia szybkich i skutecznych działań mających na celu zapobiegnięcie wyczerpywaniu się złóż fosforytów. Problem deficytu tego surowca mogą odczuć w szczególności państwa należące do Unii Europejskiej, ponieważ na terenie państw członkowskich znajdują się tylko niewielkie pokłady tych złóż. Ponadto, w chwili obecnej ich wydobycie nie jest możliwe głównie ze względów ekonomicznych oraz technologicznych.

Oczyszczalnie ścieków komunalnych posiadają największy potencjał odzysku fosforu, wykazano że ponad 90% fosforu dopływającego do oczyszczalni ścieków odprowadzanych jest w osadach ściekowych.

Piroliza osadów ściekowych nie jest nowym rozwiązaniem, do tej pory ta technologia była kojarzona głównie z odzyskiem energetycznym. W ostatnich latach zwrócono uwagę na możliwość odzysku zarówno fosforu jak i metali ciężkich zawartych w fazie stałej. Dodatkowo piroliza osadów ściekowych charakteryzuje się bardzo wysokim stopniem odzysku tego pierwiastka sięgającym 100%. Na podstawie przeprowadzonych badań można stwierdzić, że największą ilość P można odzyskać w wyniku pirolizy osadów po procesie suszenia, z terenu województwa lubelskiego może to stanowić około 1670 ton rocznie.