Phosphorus recovery from effluents of sludge treatment using sorption materials

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Abstract

The recovery of phosphorus released from excess activated sludge by sorption materials is the aim of this study. Four fine dispersion materials that are Polonite[®], dead catalyst of petroleum hydrocarbon cracking, EAF-slug and burnt dolomite were tested as means for removal of phosphorus from sludge treatment effluents. The experiments showed that burnt dolomite at 700°C is the best reactive material for this aim. In order to estimate how many less phosphorus disposals in receiving water mass balance was calculated for two scenarios. It is found that cleaning supernatant water and centrate mass phosphorus discharged into surface waters may be reduced on 56%. Overall, the results demonstrate the importance of local materials using for phosphorus recovery from effluent of sludge.

Аннотация

Целью работы является возврат фосфора возвратных потоков от обработки избыточного активного ила в производственный цикл с помощью сорбционных материалов. Для удаления фосфатов из иловой воды были использованы следующие мелкодисперсные материалы: Polonite[®], отработанный катализатор крекинга углеводородов нефти, электросталеплавильный шлак и доломит обожжённый при 700°С. Показано, что среди представленных материалов доломит является лучшим сорбентом.

Чтобы оценить, как снизится нагрузка по фосфору на водоприёмник при очистке возвратных протоков очистных сооружений канализации, был составлен материальный баланс для двух сценариев. Установлено очистка иловой воды от уплотнения и обезвоживания позволит сократить поступление фосфора в водный объект на 56%. Таким образом, показана целесообразность рециклинга фосфора возвратных потоков очистных сооружений с помощью местных сорбционных материалов.

Keywords: phosphate recovery; sewage sludge; reactive materials; wastewater

Introduction

Anthropogenic influence to global biogeochemical phosphorus cycle have led to eutrophication and exhausting the supply of phosphate rock. Nowadays, phosphorite and apatite are used to make the phosphorus-containing produce (fertilizing, detergents and other). According to the some research results (Schröder, 2010) the known resources of these minerals are estimated as enough for the next 50–125 years. Phosphorus as a key nutrient is very important for all life (Schröder, 2010). Phosphorus excess in water bodies is the mean cause of abnormal growth of algae and aquatic plants, decreasing of dissolved oxygen and biodiversity (Correll, 1998). Thus, there are required to limit export of this element to surrounding environment by recovering phosphorus from wastewater in order to support aquatic system resistance, the quality water and recycle the valuable element.

As a rule, wastewater treatment plants are the major source of water pollution. The most

common approaches for removing phosphate depending on plant capacity and requirements to waste-water discharges are enhanced biological phosphorus removal (EBPR), chemical precipitation and combination of them (van Haandel, 2007).

Chemical precipitation and EBPR lead to accumulation of phosphorus in sewage sludge. The application of coagulants that are based on Fe and Al salts results in chemical sludge, which is less appropriate for agronomic use and often must be landfilled (Metcalf, 2003). Obtained from EBPR active sludge can be used as fertilizer due to biogenic elements and essential trace elements. However a large amount of sludge can not be utilized in agriculture case of high concentrations of heavy metals, persistent organic pollutant, pharmaceuticals and etc. (De-Bashan, 2004).

Mass-balance fluxes analysis of wastewater treatment plant presents that the richest of phosphorus flows are secondary effluent and site-stream liquid obtained from sludge treatment processes (van Haandel, 2007). Under control aerobic conditions active sludge stores phosphates in solid phase. Microorganisms utilize phosphates to build the cell structure and as their energy content. The most effective wastewater treatment processes run under ratio of trace nutrients carbon BOD : nitrogen : phosphorus in waste water respectively 100:5:1. Biological phosphorus removal involves cycle of anoxic, anaerobic and aerobic conditions. Under stress conditions, as anoxic or anaerobic, phosphorus leaches from active sludge into liquid phase. Identical process takes place at the thickening, mechanical dewatering and stabilization (van Haandel, 2007).

On the one hand, phosphorus export to supernatant water is undesired event, because it leads to increasing phosphorus load on the activated sludge system. On the other hand, direct sludge utilization is limited because of content variety of pollution. So the export of phosphates into liquid sludge by followed purposely fixation in the form of bioavailable state is the perspective process (Stark, 2004). Up to date transition of phosphorus to sludge liquid under different conditions is under-investigated.

The aim of this work was to determine the number of phosphorus that can be recovered from return flows of wastewater treatment plant (WWTP) in the bioavailable form for future use.

Materials

Wastewater, suspension of active thickened sludge, centrate and supernatant water from first line at Minsk treatment plant (MTP-1, the Republic of Belarus) were examined. Suspension of active thickened sludge was collected from the bottom layer of thickener tank. Centrate is liquid phase that is separated from sludge in the centrifuge. Supernatant water is liquid fraction, which is released from excess active thickened sludge into the gravitational compaction in the thickener tank.

To remove phosphates from the supernatant water and centrate we applied four sorption materials with particle size less than 0.5 mm.

Dead-catalyst of petroleum hydrocarbon cracking (DCC) is fine dispersion grey color powder waste of the four hazard class according to Belarusian classification code. This waste arises at Mozyr oil refineries. Disperse composition of DCC is variegated, particles have a size within the range 10–100 μ m. The main component is zeolite in the catalyst of cracking and, moreover, its content can reach 40%. DCC is characterized by high mas. % of O – 50.28; Al – 25.85; Si – 21.58; La – 1.22; Na – 1.07.

Crushed electric arc furnace slug (EAF-slug) is by-product at Belarusian steel work. There are CaO – 48.04; SiO₂ – 23.34; (FeO + Fe₂O₃) – 12.13; Al₂O₃ – 9.0; MgO – 4.52; MnO – 2.98

mas. % in it average chemical composition.

Dolomite is an anhydrous carbonate mineral that is composed of calcium magnesium carbonate CaMg(CO₃)₂. Burnt at 700°C dolomite (Dolomite 700) from Ruba, Belarus, was tested in this work. The elemental composition of Dolomite 700 was follow (mas.%.): O – 37.6; Ca - 27.1; Mg - 16; Si – 2.3; Fe – 1.1; Al – 0.9; C - 15.

Polonite[®] is industrial sorbent of phosphorus that is applied in Sweden for wastewater treatment. It is manufactured from bedrock opoka at 900°C. It is know that such material has high phosphorus sorption capacity that is about 109 mg P-PO₄³⁻/g. Chemical composition is in general of (mas. %) SiO₂ – 60.1%, CaO – 25.4%, Fe₂O₃ – 2.7% μ Al₂O₃ – 5.32% (Brogowski, 2004).

Methods

Investigating influence of conditions of thickened sludge treatment on phosphorus concentration in the supernatant water investigated by experimental equipment of the volume of 2.5 liter. Sludge treatment was campaigned under aerobic and anaerobic conditions at 20°C. Furthermore anaerobic stabilization was realized with and without stirring.

Batch experiments with fine dispersion materials with dosage before 13.6 kg/m³ was performed. This range was calculated aimed on the sorption capacity. The samples were shacked for 1 hour, and then sorbent was removed by setting during 1 hour. Thereafter the phosphorus content and pH were analyzed in the purification water.

The analysis of phosphorus contents was performed spectrophotometrically, following the ascorbic acid method. The pH value was determined by potentiometric method (Rice, 2012).

Results and Discussion

In order to determination concentration of phosphates in return flows MTP-1 sample of wastewater and suspension sludge was collected. Sampling was campaign in the fives point: from grit chamber (raw wastewater), after primary settling (clarified water), from thickening tank (supernatant water), after dewatering (centrate from dewatering), and after secondary settler (purified water). The results determination of phosphate concentration and pH value are presented at the table 1.

	Date of sample collection							
Flow	5.03.2013		25.03.2013		8.04.2013		21.05.2013	
	C^1	pН	C ¹	pН	C ¹	pН	C ¹	pН
Wastewater	20.53	7.3	16.59	7.45	20.45	7.85	10.08	7.37
Clarified water	23.28	7.4	18.62	7.23	18.46	7.61	32.27	7.60
Supernatant water	76.26	7.1	92.70	7.03	63.84	6.89	145.73	7.12
Centrate	357.80	6.9	351.30	6.70	408.07	7.13	430.10	6.93
Purified water	0.34	7.2	0.72	7.20	1.93	7.43	4.02	7.47
$1 - \text{Concentration phosphates, mg PO_4^3-/l}$								

Table 1 The pH value and phosphate concentration at flows MTP-1

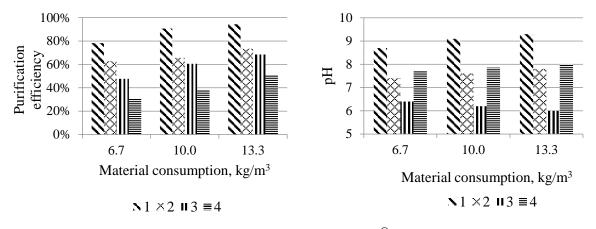
The table data gives that phosphate concentration in raw wastewater was in the range of 10– 20 mg PO₄^{3–}/l. The highest concentration of phosphates were observed in supernatant water and dewatering centrate. Concentrations in those fluxes were in ranges of 60–150 mg PO₄^{3–}/l

and 350–430 mg PO_4^{3-}/l , respectively.

The thickened sludge was exposed to anaerobic and aerobic stabilization in the experimental facilities. As a result anaerobic stabilization for 5–7 days gives fourfold increasing of phosphorus content. The highest concentration reaches 1237 mg $PO_4^{3-/1}$ out of stirring. At aerobic stabilization during 23-days the concentration gets 1185 mg $PO_4^{3-/1}$, that is fourfold more in comparison with the initial concentration. Therefore, phosphate concentration in return flows of WWTP can be regulated by operating with period of time and type of sludge treatment.

Using inexpensive local materials, that able fixing the phosphorus in a bioavailable form for plants, is a perspective variant for the removing phosphorus from returns flows of treatment plants. Consequently applying used sorption materials in agriculture will give the possibility for phosphorus to return to industrial cycle (Cucarella, 2007).

The degree of purification of centrate and supernatant water from MTP-1was determined in order to estimate material sorption parameters. Dolomite 700, EAF-slug, DCC and Polonite[®] were used to purify the centrate. The relationship between the degree of purification and pH are presented at figures 1 and 2, respectively.



1 - Dolomite 700; 2 - DCC; 3 - Polonite[®]; 4 - EAF-slug.

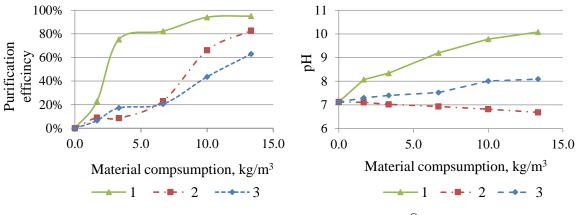
Figure 1 Phosphates removal from the liquid byproduct of centrifugation (centrate)

Figure 2 Relationship between pH and material consumption

Among the studied materials burnt at 700°C dolomite achieves the best degree of purification. Purification efficiency are grows from 78.2% to 94.5% by addition Dolomite 700 increasing consumption from 6.7 kg/m³ to 13.3 kg/m³. With Polonite[®], DCC and EAF-slug the degree of purification achieves 68.5%, 73.4% and 51%, respectively.

Increase efficiency is correlated with an increase of pH for Dolomite 700, Polonite[®] and EAF-slug. For DCC inverse relationship between pH and efficiency was observed that could be due to a different mechanism of sorption.

The results of supernatant water purification by Dolomite 700, DCC and Polonite[®] are shown at figures 3 and 4.



1 - Dolomite 700; 2 - DCC; 3 - Polonite[®].

Figure 3 Phosphates removal from the supernatant water

Figure 4 Relationship between pH supernatant water and material consumption

The presented figures data confirm also that the best sorbent is the burnt dolomite. Dosing dolomite consumption at 13.3 kg/m³ in supernatant water provides efficiency by 95%. Using DCC and Polonite[®] at similar consumption allows purification degree of 82.8% and 63%, respectively.

Therefore, the use of sorption materials for phosphorus recovery from return flows of sludge treatment facilities will reduce phosphate load on activated sludge facilities. Used materials due to their structure and properties could be utilized as ameliorant to acidic soils. It is can reduce mineral fertilizers consumption.

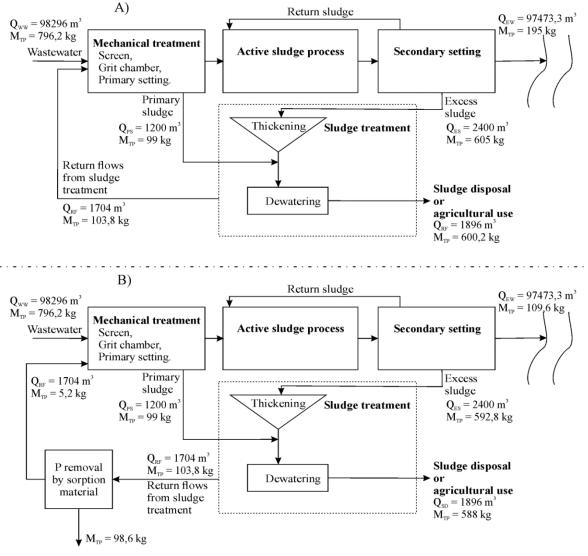
Based on experiential and reference data (Metcalf, 2003; van Haandel, 2007) phosphorus mass balance for WWTP was calculated for two scenarios: actual technology of the wastewater and sludge treatment (scenario 1 at fig. 5A) and the technology that provides phosphorus recovery from return flows by use of sorption material (scenario 2 at fig. 5B)

The calculation was performed by the following assumptions:

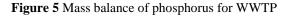
- the treatment capacity is $100\ 000\ m^3/d$;
- the phosphorus concentration in incoming wastewater is 8.08 mg P/l;

- for two scenarios the phosphorus degree of purification in the primary settling and aeration tank, the volume of return flows and phosphorus concentration there are constant;

- the degree of purification with Dolomite 700 is 95%.



A – scenario 1; B – scenario 2



Input phosphorus concentration in return flows without purification increases by 11%. So, 600.2 kg P of sludge transports to sludge bed due to scenario 1 per day.

Using sorption materials to remove phosphates from return flows in treatment plants provides an opportunity to diminish the phosphorus supplying into water bodies by 56% in comparison with scenario 1. Additionally, there is phosphorus content in the sludge decreasing. As is shown above, using the durable thickening and stabilization allow to intense phosphorus release to sludge water. In this case content of phosphorus in sludge decreases, and mass of sorb phosphorus increases.

For feasibility study the identity projects for recovering phosphorus from return flows it is important to bear in mind not only economic indicators but also the information about ecological effect (Stark, 2004). In order to choose practicable way to produce phosphorus there are carried out complex analysis based on comparison the life cycle assessment of the offered technology and producing phosphorus from nature raw materials.

Conclusion

This study shows that control the release of phosphorus during sludge treatment is important in achieving phosphorus removal in WWTP. It is shown that the result of aerobic or anaerobic stabilization is increasing concentration of phosphate in sludge liquid in 4 times. This allows increasing the phosphorus recovery from sludge water at sorption treatment.

This study was related to the sorption of phosphorus from effluent of sludge treatment by fine-dispersion reactive materials (Polonite[®], EAF-slug, DCC, and Dolomite 700) in the view of phosphorus recovery. Burnt at 700°C dolomite is the best reactive material for phosphates among tested sorbents. It is found that use Dolomite 700 to clean supernatant water and centrate mass phosphorus discharged into surface waters may be reduced by 56%.

References

Barca C., Ge'rente C., Meyer D., Chazarenc F., Andre's, Y. (2012) Phosphate removal from synthetic and real wastewater using steel slags produced in Europe. *Water Research*, **46**, 2376–2384.

Brogowski Z., Renman G., (2004) Characterization of Opoka as a basis for its use in wastewater treatment. *Polish J. Environ. Stud.* **13**(1), 15–20.

Correll D. L. (1998) The role of phosphorus in the eutrophication of receiving waters: A review. *Journal of Environmental Quality*, **2**(27), 261–266.

Cucarella V., Zaleski T., Mazurek R., Renman, G. (2007) Effect of reactive substrates used for the removal of phosphorus from wastewater on the fertility of acid soils. *Bioresour. Technol.* **99**(10), 4214–4308.

De-Bashan, Luz E., and Bashan Y. (2004) Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water research*, **38**, 4222–4246.

Metcalf, Eddy. (2003). Wastewater Engineering - Treatment and Reuse, 4th ed. McGraw-Hill, New York

Rice E. W., Baird R. B., Eaton A. D., Clesceri L.S. (ed). 2012 *Standard methods for the examination of water and wastewater*, 22nd ed, American Public Health Association, Washington, DC.

Schröder J., Cordell D., Smit A., Rosemarin A. (2010) Sustainable use of phosphorus, Report 357, Plant Research Institute, Wageningen University and Stockholm Environment Institute.

Stark K. (2004). Phosphorus recovery – Experience from European countries. In Proceedings of Polish-Swedish seminars, Stockholm June 6-8.

van Haandel A., van der Lubbe J., (2007) Handbook Biological Wastewater Treatment. Webshop Wastewater Handbook.