TESTING OF POLONITE, GAZOBETON, PAREPARE BLACK VOLCANIC SAND BEACH, AND KADIDIRI CORAL BEACH SAND FOR PHOSPHORUS REMOVAL FROM WATER AND WASTEWATER IN CONSTRUCTED WETLAND

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Abstract

Characteristics of domestic wastewater in Indonesia generally contain phosphorus 4-15 mg/L. Phosphorus in wastewater must be treated to reduce the phosphorus content according to the Indonesia: Government Regulation No. 82/2001 management of water quality and control over water pollution, maximum allowable levels is 0.2 mg/L. A 1953 report from the Max Planck Institute in Germany by Dr. Kathe Seidal discusses the possibility of using wetland plants to remove nutrients from wastewater.

The objectives of this research are to ascertain whether Polonite, Gazobeton, Parepare black volcanic sand beach and Kadidiri coral beach sand can be used as sorbent materials and to obtain the data of phosphorus sorption capacity, efficiency and phosphorus adsorption capacity constant of those materials. This research consists of batch and box experiment. Batch experiment was conducted for all material by mechanically shaking sample for several minutes with varying concentrations of the artificial phosphorus solution prepared from KH2PO4 and wastewater. Box experiment was conducted to evaluate the phosphorus removal by Gazobeton in long term experiment. The highest sorption capacity was attained by polonite 0.917 g/Kg, was followed by gazobeton 0.504 g/Kg, Parepare black volcanic sand beach 0.174 g/Kg and then the finally Kadidiri coral beach sand 0.131 g/Kg. The phosphorus sorption efficiency by Polonite, Gazobeton, Parepare black volcanic sand beach and Kadidiri coral beach sand each Kg are 91%, 50%; 17% and 13% respectively. Phosphorus adsorption capacity constant of polonite is 4906 L/g gazobeton is 115 L/g Parepare black volcanic sand beach is 19 L/g and Kadidiri coral beach sand is 14 L/g.

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1. Introduction

Characteristics of domestic wastewater in Indonesia generally contain a variety of substrates including: TS (Total Solids) 350-1200 mg/l, TDS (Total Dissolved Solid) 200-850 mg/l, TSS 100-350 mg/l, BOD (Biological Oxygen Demand) 40-400 mg/l, COD 250 -1000 mg/l, total nitrogen 20-85 mg/l, total phosphorus 4-15 mg/l, and fat 50-150 mg/l. (Khambali, 2011). According to the under section 97 of the Environmental Protection Agency Act, 1992 (No. 7 of 1992) and Indonesian Ministry of Environment Decree No. 112/2003 phosphate maximum allowable levels of 0.2 mg/L in order not to cause adverse effects to humans and aquatic environments. A 1953 report from the Max Planck Institute in Germany by Dr. Kathe Seidal discusses the possibility of using wetland plants to remove nutrients from wastewater prior to discharge into the natural environment and water body or reuse for crop irrigation (Brix, 1994).

Sadowa in Poland has horizontal subsurface flow constructed wetland that operating since 1998 to treat domestic wastewater from 150 inhabitants. The monitoring results showed a clear decrease in P removal efficiency over the eight years of operation from 96% to 24%. (Karczmarczyk and Renman, 2011).

The capacity of constructed wetlands to remove Phosphorus is a critical issue that has not yet been satisfactorily solved. Several materials have been investigated with regard to their sorption capacity. Light Expanded Clay Aggregates (LECA) was investigated by Johansson (1997). Brooks et al (2000) performed studies on wollastonite, a calcium metasilicate mineral and reported that this material is an ideal substrate for removing soluble phosphorus. Tsalakanidou (2006), discussed about the phosphate sorption capacity of improved Pollytag, clinoptilolite and two granule sizes of pumice. There has never been conducted research of Gazobeton, Parepare black volcanic sand beach and Kadidiri coral beach sand for their ability to sorp phosphorus.

Those situations makes the inspiration for the writer to test Polonite, Gazobeton, Parepare black volcanic sand beach and Kadidiri coral beach in order to ascertain whether the materials can be used as sorbent and to obtain the data of phosphorus sorption efficiency, phosphorus sorption capacity and phosphorus adsorption capacity constant of materials. Polonite has been investigated with regard to their phosphorus sorption capacity by BenjaminOpoku in 2007. The author discussed about phosphorus sorption capacity of materials through batch and column experiments conducted under laboratory conditions. Amongst the materials tested, Leca filtralite showed the highest sorption was followed by granulated Polonite and then finally the ordinary Polonite. This research has different experiment variable to the research by Opoku.

Phosphorus sorption capacity and phosphorus sorption efficiency are calculated according to the formula

$$\frac{\text{Initial P concentration (mg/L)} - \text{Final P concentration (mg/L)}}{\text{Amount of Material (g)}} \times \text{Volume (L)}$$

$$\frac{\text{Initial P concentration (mg/L)} - \text{Final P concentration (mg/g)}}{\text{Amount of Material (mg/L)}} \times 100\%$$

In order to obtain the relevant value of sorption capacity and efficiency, phosphorus adsorption capacity constant of material (K) have to calculate and the simple equilibrium equation will be used.

$$m\ (X\text{-}Xo) = V\ (Co\text{-}C) \quad (1)$$

$$X = C^{*}.\ K \quad (2)$$

Thus,

$$C = \frac{e^{\frac{Kc\,A\,t}{-V}}\ 1+\frac{V}{km} + \frac{1}{k}\ Xo+\frac{V}{m}Co}{(1+\frac{V}{km})} \quad (3)$$

A trial-and-error procedure was used for the non-linear regression method using the solver add-in with Microsoft spreadsheet. Lower values of SSE show better fit to sorption data and can give an indication of the sorption mechanism (Yahya et al, 2006).

2. Research Methodology

The research was conducted for four months in the Laboratory of Ecotechnology Water Center WULS-SGGW. Gazobeton is material building that made in cement, fine aggregate (sand, gypsum) and aluminium powder. Polonite is manufactured from the bedrock Opoka. Opoka is marine sediment belonging to a group of silica-calcite sediments (Brogowski and Renman, 2004). Most volcanic beach sands are contain lots of iron in their crystal structure which often gives rust colored appearance to volcanic rocks and sand. Quartz sand is a mineral consisting of crystals of silica (SiO2) and compounds containing impurities that carried away during the process of sedimentation. Characteristic of material is show in Table 1

Table 1. Physical Properties and Chemical properties of Sorbent materials

Material	Physical properties (Particle size)	Chemical properties	Reference
Gazobeton	2-5 mm	CaO, Na_2O + K_2O, Fe_2O_3, Al_2O_3, MgO, limestone flour, mineral powder, dolomite flour, and granulated blast-furnace slag.	http://www.Gazobeton.biz
Polonite	2-5 mm	SiO_2, CaO, Fe_2O_3, and Al_2O_3	Brogowski and Renman, (2004).
Black volcanic beach sand from Parepare	0.25 – 1 mm	Iron and minerals (olivine, pyroxene,augite, and magnetite)	http://www.sandatlas.org
Kadidiri coral beach sand	0.5-2 mm	SiO_2, Fe_2O_3, Al_2O_3, TiO_2, CaO, MgO, and K_2O	http://www.tekmira.esdm.go.id

Other Materials used in this research are potassium di-hydrogen phosphate (KH_2PO_4) and wastewater collected from constructed wetland in Sadowa. This research conducted in two type experiment: batch and box experiment. Erlenmeyer glass flask, Magnetic stirrer are specific tools that used in batch experiment. Box experiment has been done using boxes.Phosphorus removal result in batch and box experiment have been evaluated by FiaStar analysis equipment

Testing Procedure

Batch experiments were conducted by heating Opoka up to to 900^0C then all the materials have to crush, sieve and mix together with artificial solution for 15 minutes for each material other than Gazobeton. Gazobeton has three different contact times when mixing together with wastewater. Varying concentrations of the artificial phosphorus solution prepared from KH_2PO_4 were used in different initial concentrations 1, 2, 5 and 10, mg/l. During batch testing, all samples in different concentration of phosphorus were tested in triplicate. All laboratory experiments were conducted at a nominal room temperature of 20^oC. Stock volumes of the phosphorus solutions were prepared and stored in refrigerator.

Box experiments were conducted to evaluate the phosphorus removal in a long term. This experiment was carried out by filling boxes (23 cm long, 20 cm wide and 30 cm high) with the artificial phosphate solution (KH_2PO_4). Treatment of the Gazobeton in box experiment arecrushing , sieving, and covering Gazobeton with net. Gazobeton in different quantities (0g, 10g, 50g and 100 g) were wrap in a bag filter then for each bag filter put into the different boxes by hanging the bag filter. Each box was filled with the same volume of phosphate solution up to 10 L. Conductivity, pH, and dissolved oxygen have to measure time by time. Samples solution was taken three times a week for 54 days. The soluble phosphorus was measured by FiaStar analysis equipment (for Phosphate 0.1-5 mg/l PO_4 –P).

3. Results And Discussion

Batch Experiment

Phosphorus sorption capacity and sorption efficiency among of materials are show clearly in Figure 1 and Figure 2

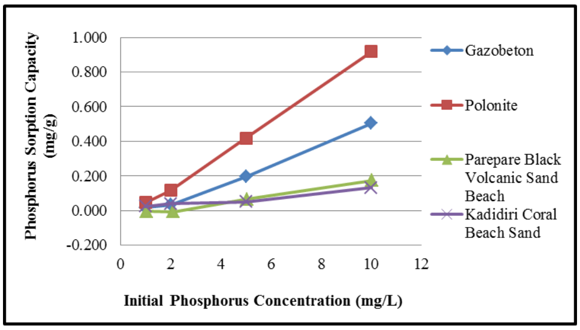

Figure 1. Phosphorus sorption capacity of sorbent materials

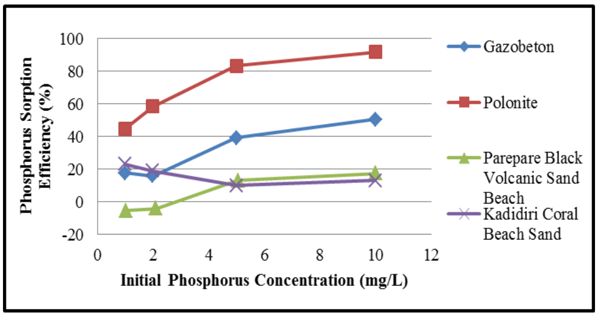

Figure 2. Phosphorus sorption efficiency of sorbent materials

Polonite demonstrated very efficient sorption of phosphorus from the nutrient solution followed by Gazobeton, Parepare volcanic sand beach and Kadidiri coral beach sand.Polonite has high capacity of phosphorus removal and sorption because Polonite has high content of CaO resulting from thermal treatment of calcium carbonate, a major component of the opoka. Adsorption the Ca2+ ions are the main phosphorus sorption processes. It has been known that Ca content correlates to the ability of a medium to remove phosphorus. In a study of Arias et al. (2001) concluded that Ca content was the most important characteristic determining phosphorus retention.

Gazobeton consist of aluminium powder (Al). It has been shown that the Fe, Al and Ca content correlates to the ability of a medium to remove phosphorus (Zhu et al., 1997). Aluminum or calcium can result in significant removal of phosphorus (Cooke, 1992; Sakadevan and Bavor, 1998; Ayoub et al., 2001; Bashan and De-Bashan, 2004). The other properties are Na_2O, and K_2O. Based on the result experiment by Tamatamah, R.A (2005) it has been known that the Na_2O, and K_2O have negative sorption value.

The negative sorption condition at low concentration of solution has occurred. Possibility for this condition could be assumed that parepare volcanic sand beach has contained phosphate thus phosphorus concentration in the water increases than the initial concentration. Due to phosphate release for the material the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is known as negative sorption. Other possibilities are Parepare volcanic sand beach has absorbed very small amount of phosphorus in 15 minutes and the precision of analysis equipment for measuring residual phosphate in solution were low.

Chemical properties of Kadidiri coral beach sand was lack of ion Fe and Al. Sorption between this material and phosphate solution is a chemical sorption caused by the presence of iron oxide (Fe_2O_3), alumina oxide (Al_2O_3) and SiO_2. Fe and Al ions on the surface of the sand will react with water molecules.

Polonite has the highest value of phosphorus adsorption capacity constant (K), it was 4906 L/g and followed by gazobeton 115 L/g, Parepare volcanic sand beach 19 L/g and Kadidiri coral beach sand 15 L/g. Phosphorus adsorption capacity constant of material is one of the critical parameter when performing laboratory experiments and have to be taken into consideration when results are used to design wastewater treatment system.

Box Experiement

The phosphorus removal by gazobeton demostrated on three boxes at different quantity of gazobeton. Phosphorus sorption capacity and phosphorus sorption effeiciency are show in Figure 3 and Figure 4.

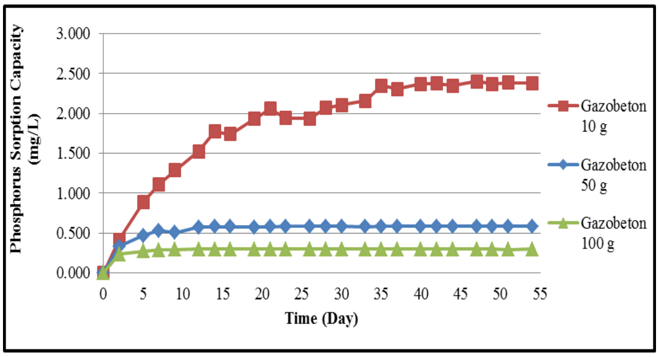

Figure 3.Phosphorus sorption capacity of Gazobeton

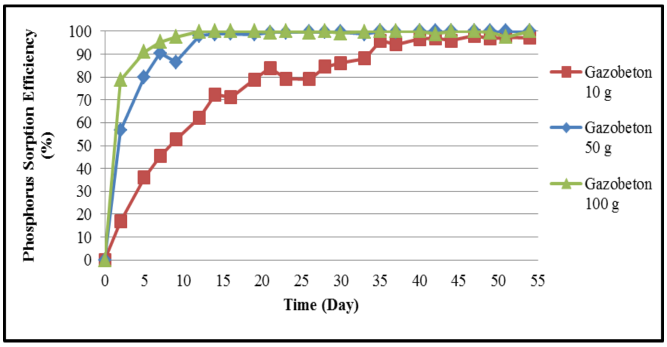

Figure 4. Phosphorus sorptionefficiency of Gazobeton

The removal tendency of gazobeton was depent on the gazobeton quantity. These results suggest predict realistic values for the average as well as the maximum phosphorus sorption capacities. A long term laboratory experiment is considered to be more realistic approach of evaluation of the sorption capacity of the substrate due to the substrate/solution ratio, the water percolate through the substrate and the substrate is repeatedly exposed to the P solution (Adam et al., 2007).

Sorption rate of gazobeton at different quantity is shows in Figure 5. Phosphorus sorption rate of 100 g gazobeton is show from the first day to the ninth day, after the ninth day of measurement the phosphorus sorption rate is close to zero and eventually equal to zero when the amount of phosphorus in solution is equal to the number posphorus on gazobeton or the equilibrium condition has occured.Gazobeton 100 g has the fastest rate of sorption then followed by gazobeton 50 g and gazobeton 10 g.

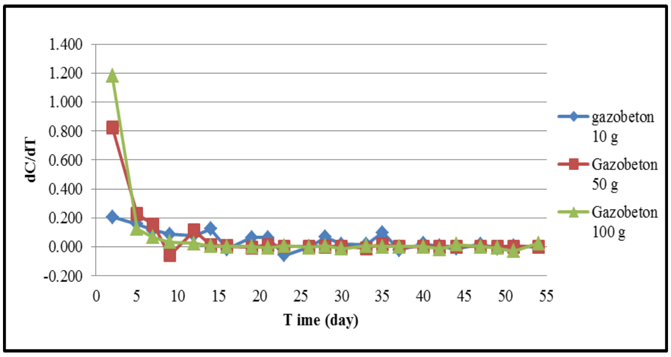

Figure 5. Phosphorus sorption rate at different quantity of Gazobeton

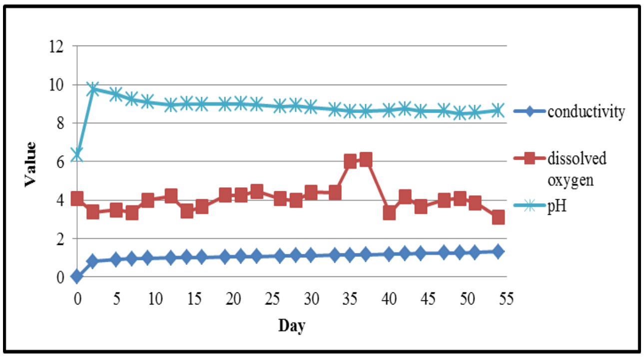

Figure 6. Statisctic in experiment Gazobeton 100 g

Box experiment method reaches the equlibrium condition for each gazobeton with diffferent quantity. The value of K for each quantity of Gazobeton show in Table 2. The final concentration in this research comes from the average value of concentration around equlibrium measurement point. The dynamic phosphorus concentration result value after equilibrium condition is resulting from hydrolisis reaction in solution and presence of other compounds that are not detected by FossSofia analysis equipment during the phosphorus analysing therefore the limitations of the analysis makes the results obtained have low accuracy.

Table 2. Phosphorus adsorption capacity constant of gazobeton in box experiment

Quantity of Materials (g)	Phosphorus concentration in solution (mg/L)	Phosphorus concentration in sorbent material (mg/g)	Phosphorus adsorption capacity constant (L/g)
10	0.063	2.384	37.558
50	0.013	0.581	44.854
100	0.006	0.299	51.484

Figure 6 shows the statistic in box experiment such as pH, conductivity and dissolved oxygen of Gazobeton 100 g. Other Gazobeton in different quantities show the almost same result for their pH, conductivity and dissolved oxygen. Soil activity in the result of measurement was lay on the range 6.33-9.01. That was the suitable pH to reach the optimal phosphorus sorption by aluminium and calcium. pH greater than 8 or 9, calcium is considered the main phosphorus removal component (Zhu et al., 1997; Richardson and Craft, 1993; Diamadopoulos and Benedek, 1984; Holford and Patrick, 1979).

The results show that with increasing weight of gazobeton initial phosphorus the conductivity were increasing day by day. The phosphorus sorption process followed by ions release, such as (OH), (H^+) and (K). an increase in ions means an increase in conductivity (Opoku, 2007).Oxygen measurements was performed to observe the changes in oxygen levels that occured during the experiment.

Fluctuation of dissolved oxygen concentration among the gazobeton in variuos weight day by day due to oxygen measurements was not conducted at a sequence time in one day but the measurement was conducted at short time and once in one day, thus the data is assumed to be constant for each measurement day. Another possibility, there has been direct contact between the surrounding with the solution that allow aerob microbes get contaminated with the solution. The presence of microbe in the solution resulted in oxygen levels decrease.

Batch and Box Experiment

Batch experiment has good indication of a material's capacity to retain phosphorus. However but did not provide the real phosphorus removal capacity in on-site systems. It is thus necessary to conduct long-term or pilot scale experiments in addition (Drizo et al., 2002; Shilton et al., 2006). Batch experiment shows that Polonite has the highest value of phosphorus adsorption capacity constant and followed by gazobeton, Parepare volcanic sand beach and Kadidiri coral beach sand. Phosphorus adsorption capacity constant of materials are 6906; 115; 19 and 14 respectivelty. Polonite has been test for long term experiment in previous researh therefore in this research, box experiment conducted only for Gazobeton.

K value for gazobeton in bacth experiment using KH_2PO_4 is 115 while gazobeton K value using wastewater is 54. The extremelly different value of gazobeton in bacth experiment is due to experiment of gazobeton using KH_2PO_4 has low ratio of material/solution and experiment conducted only in one time at very short contact time thus there is no other data that could be used in determining final K value of gazobeton. Batch experiment with a low material/solution ratio need longer time to reach equilibrium therefore batch experiments with a low material/solution ratio and a contact time in a short time will not give reliable measurements of the maximum P sorption capacity (Adam et al. 2007) as well as the value of K. 115 K value is extremely different with 54 K value, but it is still within the limits research tolerance.

Gazobeton in batch and box experiment also has different value of K. In batch experiment using wastewater, the K value of gazobeton is 54 and K value of gazobeton in box experiment is increased from 37 through 51 with increasing gazobeton quantity. The increasing value of K in box experiment is not extremely different with the K value in bacth experiment in various contact time thus K in box experiment and in bacth experiment using wastewater value is more acceptable.

The high value of phosphorus adsorption capacity constant shows the high value sorption capacity and sorption efficiency of phosphorus. The sorbent material that has the high value of K, is the good materials to remove phosphorus. On the whole of the batch and box experiment, gazobeton is the best sorbent material to remove phosphorus after plonite and then followed by Parepare volcanic sand beach and Kadidiri coral beach sand.

Economic Analysis

The economic analysis of gazobeton projects is typically carried out using the technique ofproject performance criteria such as net present value (NPV), Return of Investment (ROI) and Benefit Cost Ratio (BCR). Sadowa constructed wetland has volume 594 m3 (bed length 33 m, bed width 30 m and bed depth 0,6 m). Based on the result of box experiment, the K value is 51.484. Reducing level of phosphorus from 0.537 to 0.006 will obtain 1020 kg of gazobeton.

Total investment cost is Rp 1,067,000 ,- Operational cost isRp**.** 33,069,060,- Sales revenue productGazobeton is Rp. 33,069,060 ,-Profit (25%) is Rp.8,267,265 ,- Toal sales revenue is Rp. 41,336,325 , - Table 3. Show the cashflow calculation for Gazobeton in this research.

Table 3. Cashflow

Description	Year					
	0	1	2	3	4	5
Benefit						
Sales		41,336,325	41,336,325	41,336,325	41,336,325	41,336,325
Total benefit		41,336,325	41,336,325	41,336,325	41,336,325	41,336,325
Cost						
Investment	1,067,000					
Operational Cost		33,069,060	33,069,060	33,069,060	33,069,060	33069060
Total Cost	1,067,000	33,069,060	33,069,060	33,069,060	33,069,060	33069060
Net Benefit	**(1,067,000)**	**8,267,265**	**8,267,265**	**8,267,265**	**8,267,265**	**8,267,265**
Discount rate (6%)	1	0.89	0.8	0.71	0.64	0.57
PV	(1,067,000)	7,357,865.85	6,613,812.00	5,869,758.15	5,291,049.60	4,712,341.05
NPV						28,777,827
ROI						774.00%
BCR						1.25

Interest rate of 6% resulted to NPV Values of Rp 28,777,827 one year with value higher than zero, this means that the gazobeton business is feasible to do.Return of Investment is 774%. Benefit Cost Ratiovalue in this research is 1.25 mean that gazobeton bussines is acceptable to run.BEP is 1020 kg for one means the bussines will reach even poin after producing 1020 kg of gazobeton with an assumption that all gazobeton produced are also sold. Lower selling price will increase the amount of gazobeton to be produced and sold. In this research, gazobeton cost Rp 31,421 one kilograms resulted in 1020 Kg for the BEP. The value of BEP is a determination of production level to ensure the business to self financingand next expected to be self growing with an assumption that initial profit is equal to zero. If gazobeton can be produced and sold more than 1020 Kg one year, profit is expected.

4. Conclusions

From the results obtained it can be concluded as follows:

All the materials tested showed that all materials might be use as sorbent material to remove phosphorus from water and wastewater.

Bacth experiment shows the highest sorption capacity were attained by Polonite 0.917 g/Kg This was followed by gazobeton 0.504 g/Kg, Parepare Black Volcanic Sand Beach 0.174 g/Kg then finally Kadidiri Coral Beach Sand 0.131 g/Kg. Gazobeton using wastewater has capability to sorp less than 0.037 g/Kg of Phosphorus. Box experiment shows gazobeton demonstrated sorption capacity value lies in the range 0.583 g/Kg to 2.398 g/Kg.

The phosphorus efficiency by polonite, gazobeton, Parepare black volcanic sand beach and Kadidiri coral beach sand were 91%; 50%; 17% and 13% respectively. Gazobeton removal tendency in wastewater was less than 34 %. Very efficient 100% removal of phosphorus was reached for 50 g and 100 g gazobeton in box experiment.

The phosphorus adsorption capacity constant of polonite is 4906 L/g. gazobeton is 115 L/g. Parepare Black Volcanic Sand Beach is 19 and Kadidiri Coral Beach Sand is 14 L/g. Phosphorus adsorption capacity constant of Gazobeton using wastewater in different contact time is 54 L/g. In box experiment, phosphorus adsorption capacity constant of gazobeton lies in the range 37 L/g to 51 L/g.

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Nomenclature

A surface area of sorbent material, mm
C final phosphorus concentration in solution from equation (amount of phosphorus at solid phase / volume of solution), mg/L
C_0 initial phosphorus concentration in solution, (amount of phosphorus at solid phase / volume of solution) mg/L
C* concentration of phosphorus in solution at equilibrium condition, (amount of phosphorus at solid phase / volume of solution) mg/L
K phosphorus adsorption capacity constant of sorbent material, (amount of phosphorus at liquid phase/ amount of phosphorus at solid phase) L/g
Kc the rate constant of reaction
m mass of sorbent material, g
SSE the sum of the squared errors
t contact time, minutes
V volume of sorbent material, ml
X final phosphorus concentration, (amount of phosphorus in solid phase / amount of sorbent material), mg/g
Xo initial concentration of phosphorus in sobent material, amount of phosphorus at solid phase / volume of solution), mg/L

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