

# PHOSPHATES ADSORPTION FROM WATER BY RECYCLED CONCRETE

## ADSORPCE FOSFOREČNANŮ Z VODY RECYKLOVANÝM BETONEM

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### Abstract

It was only very recently that recycled concrete has also started to be used in water management primarily as a sorbent or reagent. Important factors influencing its use include mainly its origin, chemical, physical and mechanical characteristics. Adsorption kinetics was measured experimentally (Freundlich and Langmuir isotherm); and efficiency, values of adsorption capacity and changes of water chemical reactions due to added recycled concrete were found. Phosphates were removed either from standard solutions or from surface water.

### Abstrakt

Recyklovaný beton se díky svým vlastnostem začal v posledních letech uplatňovat i ve vodním hospodářství především jako sorbent nebo reakční činidlo. K důležitým faktorům, ovlivňujícím jeho použití patří zejména jeho původ, chemické, fyzikální a mechanické charakteristiky. Experimentálně byla zjišťována kinetika adsorpce (Freundlichova a Langmuirova izoterma), účinnost, hodnoty adsorpční kapacity a změny chemické reakce vody vlivem přidaného recyklovaného betonu. Fosforečnany byly odstraňovány jak ze standardních roztoků, tak z povrchové vody.

**Key words:** phosphates, efficiency, adsorption, recycled concrete, surface water, Freundlich and Langmuir isotherm

## 1 INTRODUCTION

Phosphates represent a form of biologically reachable phosphorus in natural waters which boldly influence eutrophication. This unwanted factor which encourages the growth of algae, blue-green algae and higher plants in flows and water basins, has negative influence on quality of water in many ways. The main sources of phosphates are mainly outflows from wastewater treatment plants, slurry from farmer fields, rain waters, etc.

Phosphates can be removed from wastewater in chemical, biological and physical-chemical ways. Those ways are very frequently combined. Chemical ways are based on phosphates precipitation with e.g. cations  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ . The precipitated phosphates are removed from water by sedimentation or flotation. In a chemical way, P<sub>c</sub> residual content in outflow of 1.0-2.0 mg/l can be easily reached. When using double precipitation, a residual content below 0.5 mg/l can be achieved, and through a high precipitant dosage, the P<sub>c</sub> residual content decreases up to value of around 0.09 mg/l. An advantage of precipitation can be seen in reaching a relatively low residual P<sub>c</sub> value and simple integration of reagents dosages in case of pre-precipitation, simultaneous precipitation or additional precipitation in a current wastewater treatment plant [1]. In biological purification, a P<sub>c</sub> residual content below 0.8-1.0 mg/l in outflow from a WWTP can be reached. The combination of biological and membranous approaches results in a very effectual variety. On membranous bioreactors, residual values are below 0.3 mg/l in outflow [1]. Physical-chemical approaches involve membranous methods, ion exchange and adsorption. In practise, the ion exchange is not used so much, while the adsorption reached a wide range of usage.

Adsorption methods are based on catching phosphates on various sorption materials. Very good results were found with a blast furnace, ash, activated bentonite, activated alumina, iron oxides, etc. The mentioned materials are mainly used as a filler of filters or a column with an inside filling in suspension [1]. During laboratory experiments, the adsorption capacity of activated clay was around 20 mg P/ 1 g of sorbent, and as for granulated ferric hydroxide it was nearly doubled.

Sorption features of the waste from ore processing were checked in a filling column [2]. The used filling items with the majority proportion of  $\text{Fe}_2\text{O}_3$  (33.1 %) had on average 68.6  $\mu\text{m}$  and an adsorption capacity 8.6 P mg/g. The adsorption capacity of granulated ferric hydroxide reached 24 P mg/g [3]. Further, the possibility of granulated water sediment was checked, in order to use it as a sorbent to remove phosphates from waste water. The detected adsorption capacity of the tested material was P mg/g [4]. The phosphates adsorption was studied on chosen natural and synthetic materials [5]. For experiments, the model  $\text{PO}_4^{3-}$  solution was used. The set values for adsorption capacities are listed below:

**Tab. 1 Summary of adsorption capacities of various materials**

Sorbent	a [mg/g]
Klinoptilolit (SR)	8.8
Chitosan – zeolit product	5.4
Klinoptilolit (CHPR)	5.6
Klinoptilolit (USA)	7.4
Bentonite	22.6
Alginit	5.2
Calsit	3.3
GEH 102	8.3
GEH 104	13.2
Slovakit	11.2
Powersorb U	4.4
Slag (CHPR)	1.0

Tab. 1 shows that bentonite has the best adsorbing capacity. Bentonite is very frequently used as isolated material for instance in waste disposal site buildings or dumps of radioactive waste. The material GEH 104 has a high adsorption capacity as well as granulated iron hydroxide which is specially produced for heavy metal adsorption mainly of arsenic from sewage.

Static tests with recycle concrete were verified under laboratory conditions by phosphates sorption on items on average 2 up to 0.063 mm [6]. Sorption effectiveness after 1 hour of agitation with an initial phosphates concentration of 100 mg/l and with neutral pH was 99 %. During these experiments, recycled concrete with a main item – tobermorite, calcium-silicate-hydrate  $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_{2.4} \text{H}_2\text{O}$  by  $\text{SiO}_2$  and  $\text{CaSO}_4$  was used. The size of the items was 0.6-1.3 mm. The experiments were carried out in a PVC column, 3.5 cm in diameter and 35 cm in height. The filling content was 140 ml (1BV - BED VOLUME (BV) - it is the total volume of filling (both solid and liquid portions together), filling height 14-15 cm. The experiments were performed with the outflow from a biological wastewater treatment plant; the average content of P, tailored in the inflow column with additional  $\text{NaH}_2\text{PO}_4$  was 10 mg/l and its COD under 15 mg/l. While the water was staying in the column for 1 hour, the rest of P was checked in the column and it was under 2 mg/l. Up to 3000 BV, the average effectiveness of P removal was 85 %, and after overcoming this mentioned content, it started to decrease. The pH value in the inflow was 7.6, in the outflow at the beginning raised up to 9.2. After 100-150 BV, the value went down below pH 9 and later up to pH 7.7. The authors decided that except the first 100 BV the water could be outflow to the recipient straight away without correcting the pH. Next, it was found out that the value of COD did not change by filtration through the recycled concrete. Effectiveness of this way was confirmed by results from a half-way operational experiment when during the first 200 BV, the efficiency of P removal was 87-99 % – that means that the P content in the inflow was 9-12 mg/l and in the outflow then 0.1-1.3 mg/l [7]. The overview shows the capacity of various materials which were used as a content of a root zone wastewater treatment plant with respect to phosphates removal from sewage [8]. The materials were divided into three groups – natural, (e.g. alunit, apatit, bauxit, slate, marl, dolomit, zeolite, etc.), industrial (e.g. ash, blast furnace slag, portland cement, etc.), and synthetic (e.g. Filtra P, Filtralite PTM, Leca, LWA, etc.). The values of maximum adsorption capacities of couples of materials from each group are listed below.

**Tab. 2 Maximum values of adsorption capacities of two chosen materials from each group**

Group	Max. adsorption capacity [P mg/g]	Ca content (CaO) [%]	Sort of material
Natural materials	40	30.1 (42.1)	marl
	5.2	21.7	dolomite
Industrial materials	420	-	blast furnace slag
	65	20.9 (29.2)	ash from slate
Synthetic materials	12	-	laboratory prepared
	3.5	46.5	low molecular weight aggregates

The authors observed an increase in the P adsorption capacity in various materials when the content of CaO raised up.

The efficiency of phosphates from surface waters was compared using natural and engineering materials. [9]. The sludge correction from mine water treatment, steelworks sludge, aluminium and ferric sludge from water treatment, ash, limestone and biologically produced oxides Fe in low-budget and engineering materials were investigated. For example, the sludge from mine water treatment gave the opportunity to release the content of P up to 50 µg/l with a capacity of 40 000 m<sup>3</sup>/m<sup>3</sup>. The removal of phosphates from water using the mentioned materials depends probably on two main processes, in particular adsorption and precipitation. The adsorption takes place on the outer surface of materials and ties are born between PO<sub>4</sub><sup>3-</sup> and metal oxides. The condensation takes place between PO<sub>4</sub><sup>3-</sup> and present actions Ca<sup>2+</sup> and Mg<sup>2+</sup> with the creation of sparingly soluble compounds which fall from the water in a form of precipitate. A high content of natural organic substances can influence the phosphates stripping from the water in a negative way, mainly by blocking adsorption places on the material surface.

The target of this article is to present laboratory tests with recycled concrete as a sorbent and a reaction agent in removing phosphates from waste water, mainly in a small wastewater treatment plant.

## 2 MATERIALS AND METHODS

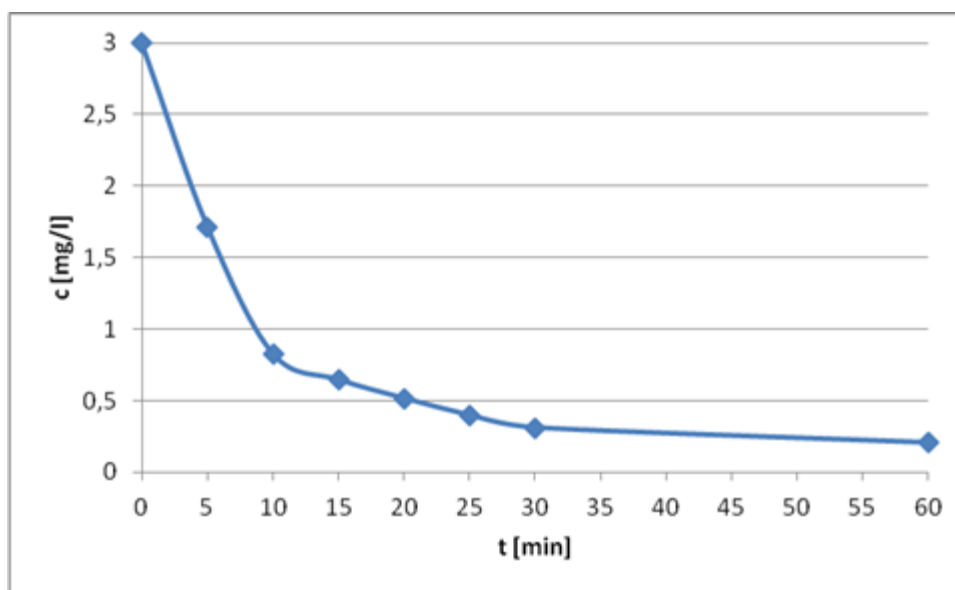
The study itself focused on checking sorption features of recycled concrete during phosphates removal from water. Recycled concrete aggregates from railroad ties having different grain sizes, a model solution prepared from anhydrous KH<sub>2</sub>PO<sub>4</sub> in distilled water, and surface water disposable taken from the Vltava River were used. The phosphates content in samples was detected by the absorption spectrophotometry after a reaction with molybdate and a reduction with ascorbic acid. [10] Each experiment was repeated three times with each fraction of recycled concrete and in order to draw conclusions, average values of results were used. The adsorption time was 1 hour. The chemical analysis of recycled concrete is shown in Tab. 3.

**Tab. 3 Main features of chemical composition of recycled concrete**

Pointer	[%]				
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
	38.30	10.70	20.60	3.70	0.12

### 3 RESULTS AND DISCUSSION

At the beginning of the laboratory experiments, the necessary time to attain equilibrium was detected. We used a recycled concrete fraction of 0.125-0.250 mm and model water ( $\text{PO}_4^{3-}$  3.0 mg/l). The results of the experiments at laboratory temperature are shown in Fig. 1.



**Fig. 1 Adsorption capacity (recycled concrete fraction – 0.125-0.250 mm)**

As shown in Fig. 1, the largest reduction in phosphate concentrations came in the first ten minutes of the experiment. The equilibrium concentration was reached roughly in 60 minutes. This time was used further in the next experiments with recycled concrete of various fractions when their efficiency and adsorbing capacities were identified.

The results of the experiments, focused on the comparison of phosphates adsorption efficiency by various fractions of recycled concrete, are shown in Tab. 4. The used model solutions were graded in their  $\text{PO}_4^{3-}$  concentrations from 0.2 up to 3.0 mg/l, the time of adsorption was 60 min.

**Tab. 4 Adsorption efficiency of phosphates by recycled concrete**

Fraction [mm]	$c_0$ [mg/l]	0.2	0.5	1.0	1.5	2.0	3.0
0.000 - 0.063	Efficiency [%]	87.54	93.44	96.46	98.16	97.64	88.72
0.063 - 0.125		81.30	91.87	93.83	95.45	89.04	95.10
0.125 - 0.250		63.92	82.16	84.91	86.01	86.68	89.50
0.250 - 0.500		10.25	13.14	13.67	10.00	20.43	37.90
0.500 - 1.000		0.00	3.70	5.80	18.31	27.05	43.54
1.000 - 2.000		0.00	0.00	0.00	0.71	10.33	30.95

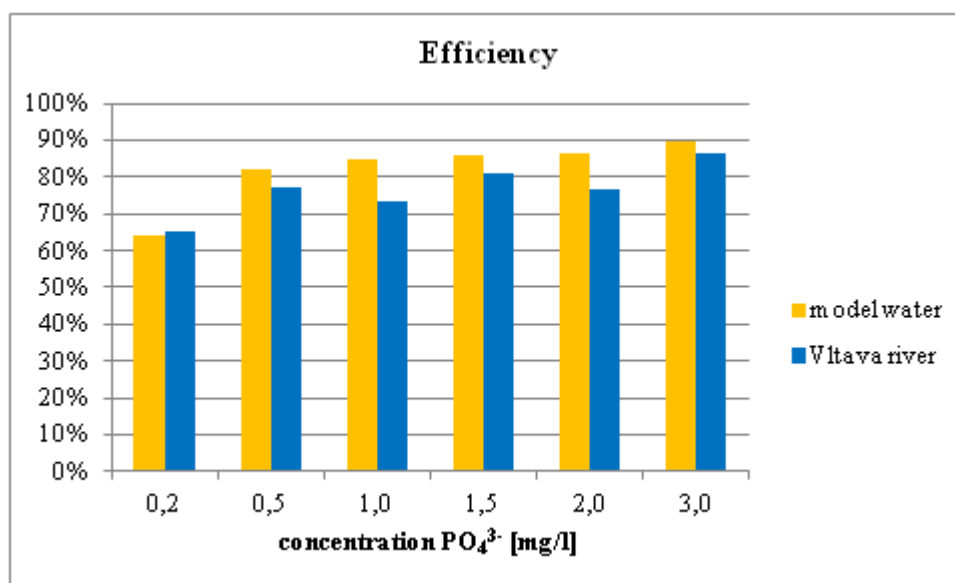
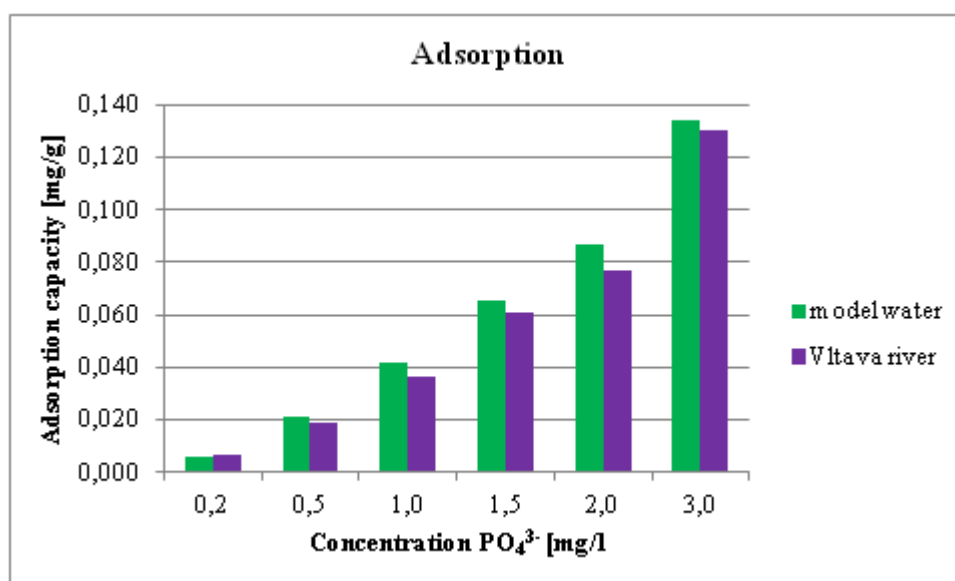
When comparing the results from the experiments, it can be found that if the fraction of recycled concrete rises up, the efficiency of phosphate removal goes down. The efficiency was influenced by the phosphate concentration in water as well. The larger it was, the higher values were reached. Only in the fractions of 0.5-1.0 mm and 1.0-2.0 mm with a water content of 0.2 up to 1.0 mg/l, zero efficiency was detected.

In order to find out the phosphate adsorption capacity for various fractions of recycled concrete, the experiments were performed with model water and repeated three times. Average results are shown in Tab. 5.

**Tab. 5 Values of phosphate adsorption capacity by various fraction of recycled concrete**

Fraction [mm]	$c_0$ [mg/l]	0.2	0.5	1.0	1.5	2.0	3.0
0.000 - 0.063	a [mg/g]	0.009	0.023	0.048	0.074	0.098	0.133
0.063 - 0.125		0.008	0.023	0.047	0.072	0.089	0.143
0.125 - 0.250		0.006	0.021	0.042	0.065	0.087	0.134
0.250 - 0.500		0.001	0.003	0.007	0.007	0.020	0.057
0.500 - 1.000		0.000	0.001	0.003	0.014	0.027	0.065
1.000 - 2.000		0.000	0.000	0.000	0.001	0.010	0.035

To what level the character of water can influence the adsorption process of phosphates – it was find out on the sample of the surface water from the Vltava River. The concentration of  $\text{PO}_4^{3-}$  was adjusted to the same value as in the model water. The comparison of the results from the experiments with fractions of recycled concrete of 0.125-0.250 mm is shown in Figs 2 and 3.

**Fig. 2 Comparison of the recycled concrete efficiency of the model and Vltava River waters****Fig. 3 Comparison of the  $\text{PO}_4^{3-}$  adsorption by recycled concrete in the model and Vltava River waters**

As shown in Figs 2 and 3, the adsorption efficiency reached in the Vltava River water was by 2-3 % lower than in the model water when using the same fraction of recycled concrete of 0.125-0.250 mm. It could be caused by the presence of organic substances which decrease the adsorption capacity of the used material.

The main experiments were focused on setting the adsorption capacity of recycled concrete and adsorption kinetics (Freundlich and Langmuir isotherms).

The relation below was used:

$$a = \frac{V(c_o - c_r)}{1000m} \quad (1)$$

Where:

- $a$  – Adsorption capacity [mg/g],
- $c_o$  – Initial phosphates concentration [mg/l],
- $c_r$  – Phosphates concentration after reaching balance [mg/l],
- $m$  – Weight of recycled concrete [g],
- $V$  – Volume of solution [l].

For the quantitative description of the dependence  $a = f(c_r)$ , adsorption isotherms according to Freundlich and Langmuir were used as follows:

$$\text{Freundlich isotherm } a = Kc_r^n \quad (2)$$

$$\text{Langmuir isotherm } a = a_m \frac{bc_r}{1 + bc_r} \quad (3)$$

Where  $K$ ,  $n$ ,  $a_m$ ,  $b$  are constants depending on temperatures and characteristics of three substances – solvent, solute and recycled concrete ( $K = 0.004267$ ,  $n = 0.555031$ ,  $a_m = -24.57$ ,  $b = -0.00348$ ). The constant values were set experimentally.

A graphic expression of isotherms is shown in Figs 4 and 5.

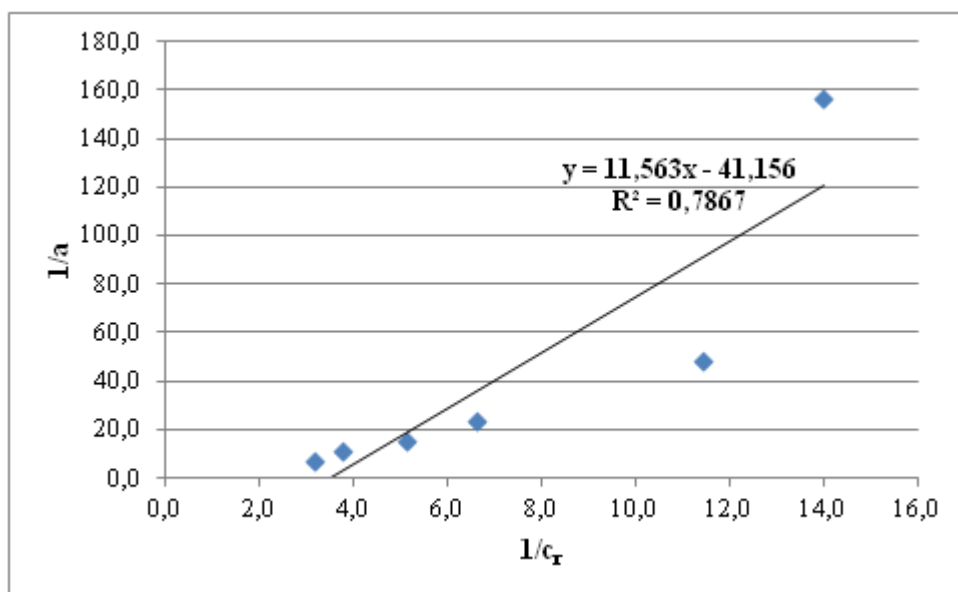
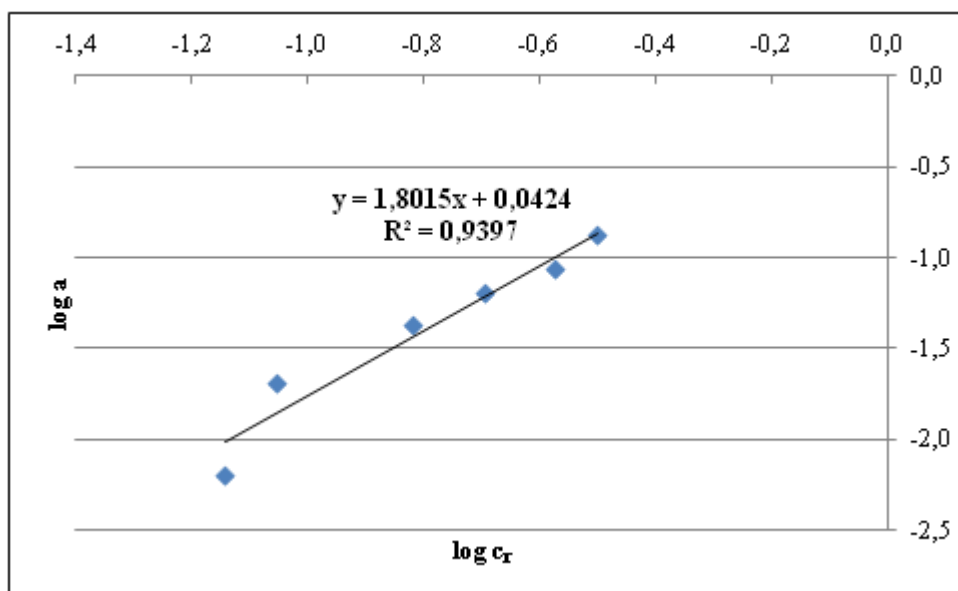


Fig. 4 Langmuir isotherm



**Fig. 5 Freundlich isotherm**

The lines through the right points in coordinates show that either Langmuir or Freundlich isotherms are usable for an analytical expression of  $\text{PO}_4^{3-}$  adsorption mechanism (concentration range of 0.0-3.0 g/l) on recycled concrete.

Recycled concrete in contact with water changes its chemical reaction. The check was again carried out using the Vltava River water with its pH of 7.39 before the experiment. Tab. 6 shows the results of the experiment, during which the pH values were measured after melting 10 g of recycled concrete – fraction 0.125-0.250 mm with 500 ml of the Vltava River water in defined intervals.

**Tab. 6 Change of pH depending on time**

Time [min]	0	30	60	120	180	240
pH	10.30	11.10	11.25	11.32	11.33	11.32

Tab. 6 shows that the pH increased from a previous value of 7.39 up to 10.3 immediately after mixing the water with recycled concrete. During agitation lasting next 30 minutes, the pH increased up to 11.1. Roughly after 60 minutes, the pH value got settled at 11.3.

#### 4 CONCLUSIONS

All reached laboratory results show that recycled concrete presents a real alternative solution for the phosphate removal from water. This attitude can be applied to a small wastewater treatment plant, especially in a range of tertiary wastewater treatment options. For the standard phosphates liquid, the best sorbent was recycled concrete, especially its fraction of 0.125-0.250 mm with a checked  $\text{PO}_4^{3-}$  adsorption capacity from 0.006 up to 0.134 mg/g. Very good results were reached in phosphates adsorption from surface (Vltava River) water. A disadvantage of the recycled concrete as a sorbent can be seen in that it increases the water pH over 11 in contact with water. The application of phosphate removal from waste water assumes additional neutralization of cleaned water before its release to the recipient.

#### ACKNOWLEDGMENT

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