Environment Protection Engineering

Vol. 31 2005 No. 1

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THE INFLUENCE OF A CONSTANT ELECTROMAGNETIC FIELD ON PHOSPHORUS REMOVAL FROM WASTEWATER IN METAL PACKING SYSTEMS

The possibility of using electromagnetic field (EMF) in order to achieve more efficient phosphorus (P) reduction in wastewater treated in metal packing systems was investigated. The waste made of powdered milk and typical domestic sewage from municipal sewers were used in the experiment. The impact of the kind of digested metal (Al, Fe) on the effectiveness of the phosphorus compounds (P–PO_4, P_{tot}) and organic compounds (COD) reduction was determined. Moreover, the importance of the EMF in a decrease in the concentration of these compounds was investigated. The most efficient was the system that combined simultaneously physical factor and steel filling. This technological variant seems to be the most effective as it allows us to remove from 38% to 98% of total phosphorus and from 10% to 63% of COD, depending on the retention time. A 48-hour retention time made it possible to remove the whole amount of phosphorus (P–PO_4) from the sewage treated.

1. INTRODUCTION

A lot of well-known methods of phosphorus limitation in wastewater are applied on a large scale. These methods are based on the activity of bacterial strains that assimilate phosphorus compounds (P–PO_4) for their growth and biomass increase and in such a way limit phosphorus concentration in wastewater [1], [2], [3], [4]. Another equally popular methods of phosphorus removal involve introduction of chemical reagents to the systems. They allow precipitation of phosphate ions from the solutions in the form of slightly soluble salts. Aluminium (Al), iron (Fe) and calcium (Ca) salts are considered to be the most common precipitants [5].

In practice, however, the use of these methods is quite troublesome. Activated sludge methods, for example, are pretty complicated. Moreover, microorganisms have to live under strictly defined aerobic/anoxic conditions. Besides, the bacteria of acti-

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vated sludge are sensitive to the concentration of the influents and wastewater pollutants as well as toxic substances [2], [4]. Chemical precipitation, although extremely effective in wastewater treatment, is quite expensive and responsible for an increase in sludge mass [6].

Therefore there is experienced an urgent need for quite new, effective systems that allow an efficient removal of phosphorus and organic compounds from wastewater. Independent systems for effective treating the wastewater as well as modernization and improvement of the existing wastewater treatment plants are desirable. Due to an improvement of wastewater treatment it is possible to implement the technologies that take advantage of clear forms of metals and a wide range of the physical factors [7], [8], [9]. The impact of the ultrasounds, microwaves, electrical current, and UV or gamma radiation was tested. It is proved that electromagnetic field (EMF) intensifies coagulation and organic compound biodegradation with the use of the activated sludge and under specific conditions can be one of the elements that determine effective pollutant removal [9], [10]. However, the assessment of the mechanism and the impact of EMF on the nutrient concentration in the solutions is quite rarely the subject of investigations.

The aim of the experiment was to determine the influence of the electromagnetic field (EMF) on the efficiency of removal of phosphorus (as $P–PO_4$, P_{tot}) and organic compounds (as COD) from wastes in the metal packing systems.

2. MATERIALS AND METHODS

The waste made of powdered milk and typical domestic sewage from municipal sewers were used in the experiment. The composition of wastewater used in the experiment is shown in table 1.

Table 1

Characteristics of the wastewater used in the experiment

Parameter	Unit	Wastes made of powdered milk	Domestic sewage
COD	mg O_2/dm^3	538.1	154.3
BOD_5	mg O_2/dm^3	427.2	82.4
$N_{tot.}$	mg N/dm^3	37.4	49.7
$N–NH_4$	mg $N–NH_4/dm^3$	0.7	26.1
$P_{tot.}$	mg P/dm^3	7.83	5.24
$P–PO_4$	mg P/dm^3	2.97	4.39
Reaction	pH	7.03	6.97
Al	mg Al/dm^3	0.10	0.12
Fe	mg Fe/dm^3	0.02	0.08

Investigations were carried out in three stages in a static system being equivalent to a laboratory scale. The technological systems used in the each part of the experiment were different. All analyses were conducted at ambient temperature of 20 ºC.

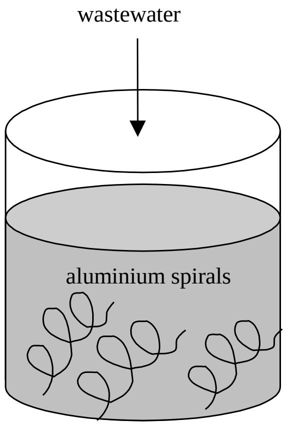


Fig. 1. Scheme of the experimental set-up in the first stage of the experiment with aluminium packing

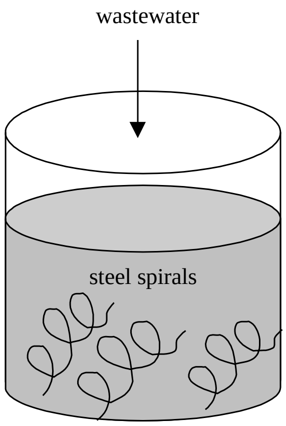
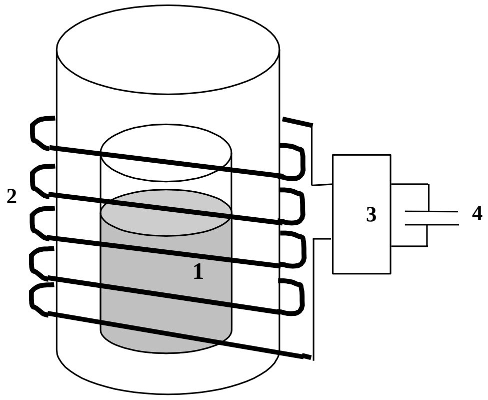


Fig. 2. Scheme of the experimental set-up in the first stage of the experiment with steel packing

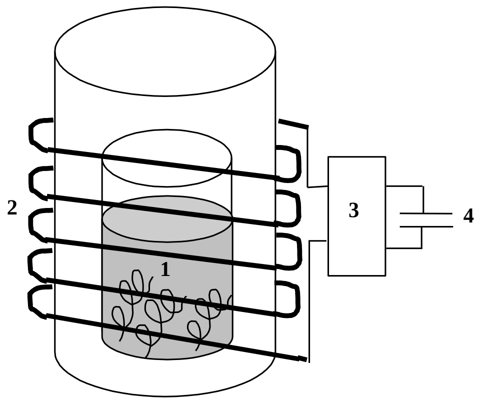
In the first stage of the experiment, the impact of the metal packing, the only factor that limits the pollutants concentration, on the waste treatment was analysed. Aluminium packing was used in the first series (figure 1), and steel packing in the second one (figure 2). In both series, the solutions to be treated were supplied to the model reactors, each of 1 dm^3 volume. Metal parts of the reactors were wire spirals whose contact surface with wastes approached 215 cm^2.

In the second stage of the experiment, only the impact of EMF on the pollutant concentration in the analysed wastes was determined. Wastes were supplied to separate reactors and exposed to a direct influence of the EMF (figure 3).



1. The model reactor without metal packing
2. Electromagnetic coil
3. Electromagnetic disintegrator
4. Source of current

Fig. 3. Scheme of the experimental set-up in the second stage of the experiment



1. The model reactor without metal packing
2. Electromagnetic coil
3. Electromagnetic disintegrator
4. Source of current

Fig. 4. Scheme of the experimental set-up in the third stage of the experiment

In the third stage, metal packing and EMF were used simultaneously in the technological system. Depending on the series, the packing of an appropriate material was introduced in the reactor filled with a definite volume of wastes which were then exposed to a direct influence of the EMF (figure 4). The first series of this experimental stage involved the impact of the aluminium packing on the phosphorus removal from wastes. In the second series, the efficiency of the treatment process with steel packing was analysed.

A basic experimental device was a cylindrical container made of plastic material and of the diameter of 200 mm and the height of 740 mm. Electromagnetic coil was wound on its circumference. The coil was joined to the electromagnetic disintegrator which guarantees a specific current frequency and a proper radiation intensity (figure 4). The wastes were introduced to laboratory glass reactors and exposed to EMF. The experiment in two final stages was carried out at the current frequency f of 10.0 kHz and at radiation intensity Φ of 100.0 μWb.

Table 2

Methods of controlling of chemical parameters

Parameter	Method
$P_{tot.}$	Acid persulfate digestion method (adapted from *Standard Methods for the Examination of Water and Wastewater*, USEPA approved for wastewater analysis)
$P–PO_4$	Molybdovanadate method with AccuVac reagent solution (adapted from *Standard Methods for the Examination of Water and Wastewater*)
COD	Reactor digestion method (USEPA approved for wastewater analysis)
Fe	FerroVer method (USEPA approved for wastewater analysis)
Al	Aluminum method (adapted from *Standard Methods for the Examination of Water and Wastewater*)

Each series of the investigations was repeated three times and in figures and tables the average results of the analyses are shown. After 3, 24 and 48 hours of the experiment the waste samples were analysed for the changes in $P–PO_4$, P_{tot} and organic compound concentrations expressed as COD. Additionally iron and aluminium concentrations and induced currents generated on the packing surface were controlled in the first and third stages of the experiment (table 2). Chemical parameters were determined using HACH DR/2000 spectrophotometer. Induced currents were controlled with a measuring instrument ISO – TECH IDM 69. Wastewater content was also analysed in control samples treated without packing and EMF. Finally the quality of wastes being exposed to EMF and treated in the presence of packings was compared with the quality of control wastes.

3. RESULTS

The concentrations of the pollutants in wastes in the control samples that were neither exposed to EMF and nor treated in the presence of metal packing decreased with time but in a quite narrow range. The decrease in COD concentration ranged from 3% to 5% after 24 hours and from 10% to 15% after 48 hours of tratment. The decrease in a total concentration of phosphorus was observed but it varied, depending on the type of wastes. After 48 hours the removal of total phosphorus from domestic wastes and wastes made of powdered milk approached 6% and 12%, respectively.

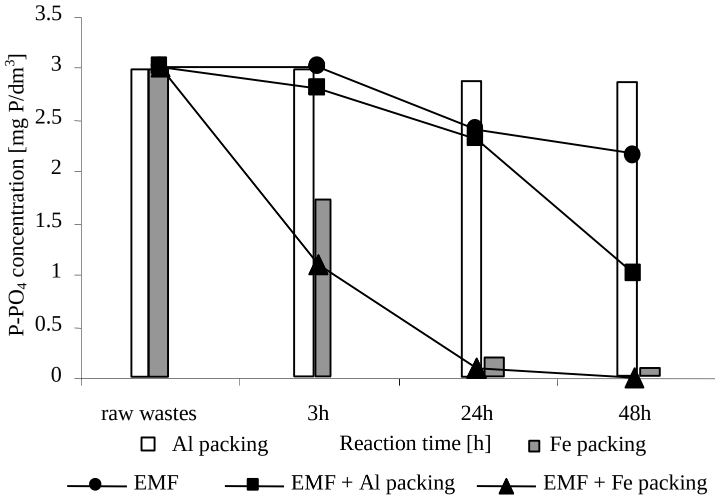


Fig. 5. Changes of P–PO_4 concentration in the wastes made of powdered milk

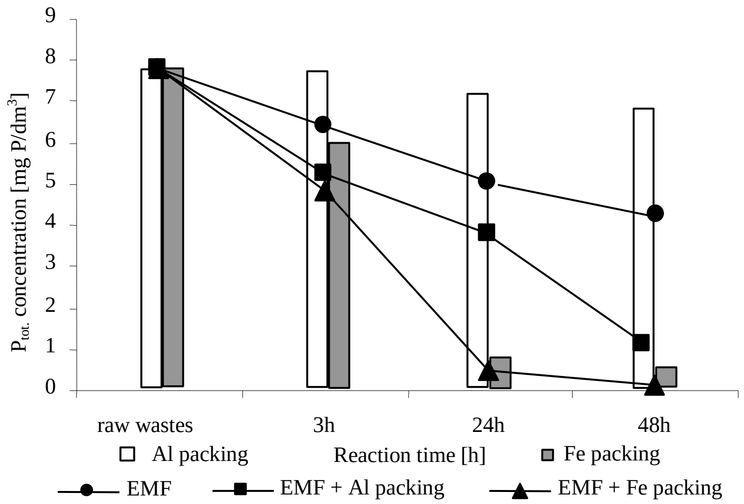


Fig. 6. Changes of $P_{tot.}$ concentration in the wastes made of powdered milk

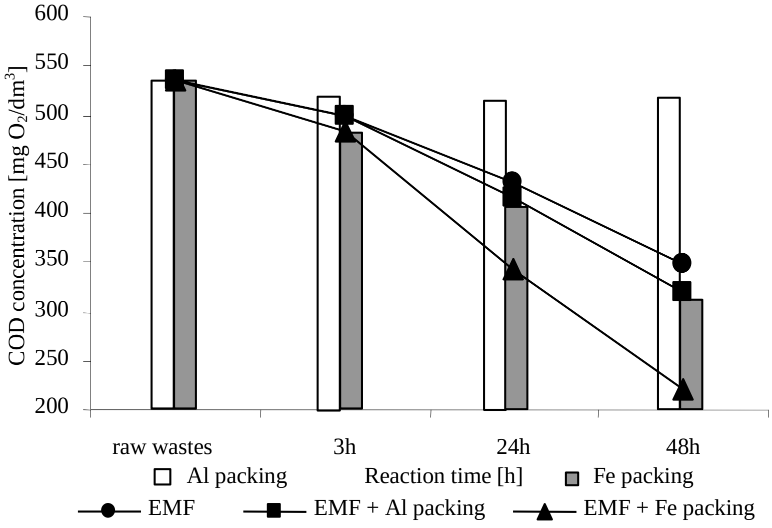


Fig. 7. Changes of COD concentration in the wastes made of powdered milk

Table 3

Changes in the concentration of metals during the first stage of the experiment with the metal packing

Reaction time [h]	Al concentration [mg/dm^3]		Fe concentration [mg/dm^3]	
	Wastes made of powdered milk	Domestic sewage	Wastes made of powdered milk	Domestic sewage
Raw wastes	0.10	0.12	0.02	0.08
3	0.10	0.12	6.81	10.30
24	0.11	0.12	8.42	14.42
48	0.11	0.11	22.14	29.00

In the first stage of the experiment, the impact of two types of metal packing on the efficiency of pollutants removal was assessed. The spirals made of aluminium wire did not change considerably the parameters analysed. Neither the wastewater prepared from powdered milk nor domestic sewage showed significant changes in the pollutant contents even after 48 hours of treatment. In the case of diary sewage, the removal of P–PO_4 and total phosphorus was as high as 4.7% (figure 5) and 12.5% (figure 6), respectively; however, the efficiency of COD removal reached 3% (figure 7). Similar efficiency of the waste treatment was obtained for domestic wastes (figures 8–10). There was no corrosion of packing metal, and aluminium ions were not released to the solution. Aluminium concentration did not change during the whole cycle of the treatment (table 3). Steel wire packing appeared to be more effective, since it allowed much better reduction of both phosphorus forms and COD just after three hours of the experiment. In domestic wastes, the efficiency of P–PO_4 removal was almost 100% (figure 8) and that of P_{tot} approached 98% (figure 9). After 48 hours of the treatment the COD reduction was 36% (figure 10). In the case of waste prepared from powdered milk, the treatment effects were slightly worse (figures 5–7). Finally, the effluent contained 0.092 mg P/dm^3 in form of P–PO_4, 0.473 mg P/dm^3 in form of total phosphorus and 313 mg O_2/dm^3 (COD). It was found that iron corrosion in the solution of domestic sewage was much more intensive (table 3).

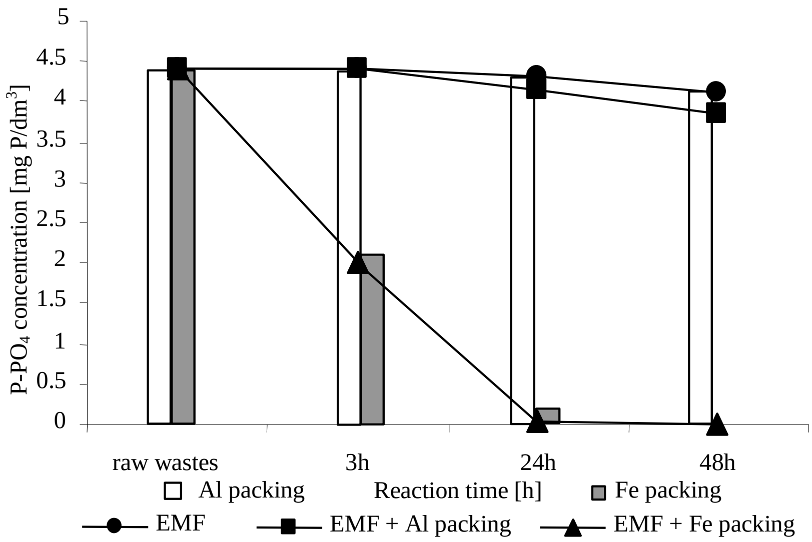


Fig. 8. Changes of P–PO_4 concentration in domestic sewage

In the next stage, only EMF effect was investigated. In such a case, the removal of pollutants along with prolonging the retention time was observed. After 3 hours of treatment there was observed only a slight loss of phosphorus in dairy wastes (figures 5–6). The concentration of pohosphate forms was the same, but that of total phosphorus decreased to 6.4 mg/dm^3. Further analyses proved that both phosphorus forms were continuously removed. Finally, after 48-hour treatment the solution contained 2.25 mg P–PO_4/dm^3 (figure 5) and 4.5 mg P_{tot}/dm^3 (figure 6). The removal efficiency of COD was 35% (figure 7). In the case of domestic sewage, phosphorus changes were slower. An insignificant removal of both forms of this nutrient was observed just after 24 hours and 48 hours of the experiment (figures 8–9). EMF caused an effective COD reduction. The value of COD decreased to 79.2

mg O_2/dm^3 at its initial concentration of 154.3 mg O_2/dm^3 (figure 10).

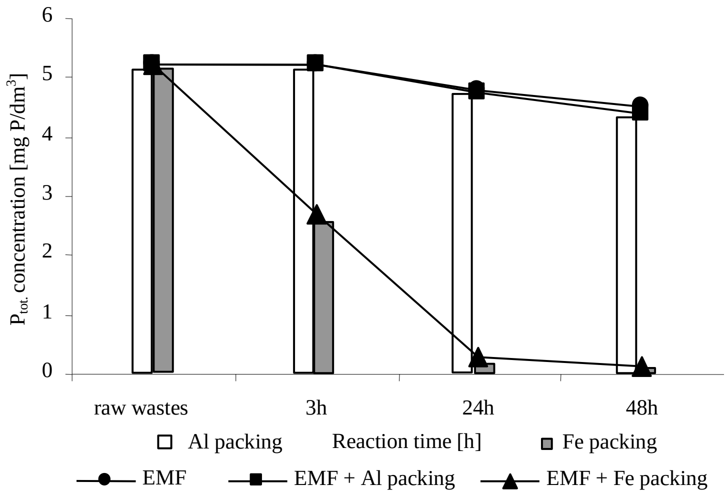


Fig. 9. Changes of $P_{tot.}$ concentration in domestic sewage

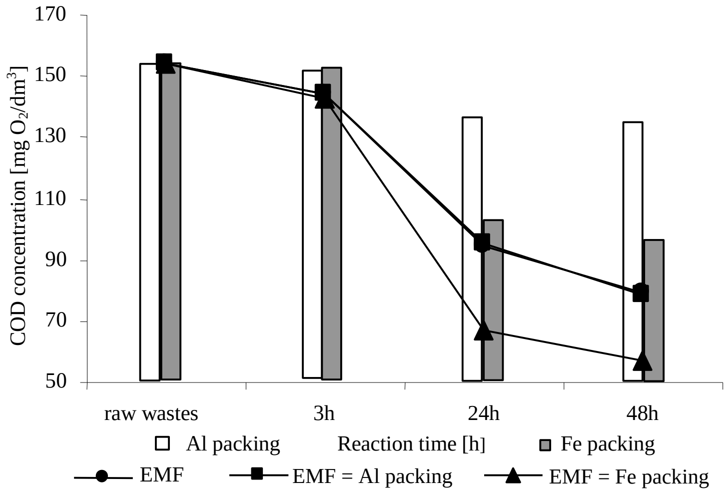


Fig. 10. Changes of COD concentration in domestic sewage

In the third stage of treatment, metal packing and EMF were used simultaneously (figure 4). At first the impact of the aluminium packing on the pollutant removal was assessed. It improved removal of phosphorus and COD from both wastes (made of powdered milk and domestic sewage). After 48 hours in one dm^3 of a dairy waste the concentration of $P–PO_4$ (figure 5), P_{tot} (figure 6) and oxygen (figure 7) reached 1.0, 1.32 and 320 mg, respectively. After 48-hour retention in domestic sewage the concentration of P–PO_4 was 3.84 mg/dm^3 (figure 8), that of P_{tot} – 4.40 mg/dm^3 (figure 9) and that of COD – 78.6 mg O_2/dm^3 (figure 10). A simultaneous use of EMF and steel packing gave better results, especially in the case of COD reduction. A final value of COD in wastes prepared from powdered milk reached 220 mg O_2/dm^3 (figure 7), while in domestic sewage was 56.8 mg O_2/dm^3 (figure 10). In both kinds of wastewater just after 24 hours, the concentration of P–PO_4 approached zero and after 48 hours this form of phosphorus was no longer present in the samples analysed (figures 5 and 8). The removal of a total phosphorus was similar. In dairy wastes, its concentration after 24 hours decreased to 0.49 m/dm^3 and after 48 hours it decreased continuously to 0.00 mg/dm^3 (figure 6). Similar results were obtained for domestic sewage: The concentration of total phosphorus decreased to 0.1 mg/dm^3 (figure 9). High secondary pollution of both kinds of wastes with iron ions was observed. In domestic sewage, iron reached the concentration of 51 mg/dm^3 after 48 hours (table 4).

Table 4

Changes in the concentrations of metals during the third stage of the experiment with the metal packing and EMF

Reaction time [h]	Al concentration [mg/dm^3]		Fe concentration [mg/dm^3]	
	Wastes made of powdered milk	Domestic sewage	Wastes made of powdered milk	Domestic sewage
Raw wastes	0.10	0.12	0.02	0.08
3	0.10	0.12	8.95	14.30
24	0.12	0.10	15.50	30.40
48	0.11	0.10	33.00	51.00

In our experiment, high corrosion rate of steel and intensive iron leaching to the wastes treated were observed. These processes were more effective in the system with electromagnetic field (tables 3 and 4). Inductive currents on the packing surface seem to be responsible for this phenomenon. It was proved that the intensity of inductive currents ranged from 0.4 μA to 18.5 μA for metal packing, depending on the kind of wastes and the sort of metal. Higher values of inductive currents intensity were generated in steel packing under dairy wastes conditions (table 5).

Table 5

Changes of the inductive currents' intensity during the third stage of the experiment with the metal packing and EMF

Reaction time [h]	Inductive currents' intensity [μA]			
	Aluminium packing		Steel packing	
	Wastes made of powdered milk	Domestic sewage	Wastes made of powdered milk	Domestic sewage

3	0.5	0.5	18.5	16.7
24	0.5	0.4	15.3	10.7
48	0.5	0.6	10.8	9.7

4. DISCUSSION

The aim of our investigations was to assess the effectiveness of the phosphorus and COD removal stimulated by packing systems and EMF. Metals (Fe, Al) in clean, ion forms are supplied to wastewater. Contrary to the technologies which are based on coagulants in the form of salts, this method makes the limitation of chemical reagents possible.

The experiment results showed that steel packing was much more effective in phosphorus removal than aluminium packing. The methods that apply the technique of clear iron leaching to wastewater treatment technologies have widely been used recently. Activated filter filled with gravel or sand packing that is covered with $Fe(OH)_2$ or filter with steel packing can serve as the examples. The tests with gravel filter revealed its usefulness. Phosphorus reduction in such conditions ranged from 34% to 78%, depending on hydraulic conditions. The effectiveness of the filters without iron hydroxide in the removal of phosphorus compounds was 6.4% [11]. Similarly high treatment efficiency was achieved for plant filter with metal packing working on a laboratory scale at wastewater treatment plant in Nowy Most, Poland [12].

Phosphorus ($P–PO_4$) from tap and ground water was removed in the columns equipped with filters filled with sand or olivine being covered with iron or aluminium hydroxide. The effectiveness of the treatment process was over 90% and final $P–PO_4$ concentration was as low as 0.05 mg/dm^3 [13]. It was proved that the technologies described allow iron ions leaching in wastewater conditions. Therefore it seems purposeful to carry out the tests aiming at improvement of the metal ions leaching in the solutions treated, which directly affects the phosphorus removal from wastewater.

This effect can be enhanced by electrochemical metal leaching in technological systems which is confirmed by the results of water and wastewater treatment. Electrocoagulation consists in metal ion leaching to the solution by means of electrolytic leaching in electrode. We compared the efficiency of phosphorus removal and energy consumption in electrocoagulation, depending on the type of electrode (aluminium or iron). The tests indicated that aluminium electrode enhanced the process effectiveness and reduced an energy consumption. Under optimal conditions phosphorus reduction reached 95% [8].

The method described in this paper is based on similar mechanisms but leaching of metal ions is spontaneous and due to electromagnetic field use. The results obtained differ from these described above. The phosphorus removal as a result of metal leaching is effective only at steel packing. The aluminium corrosion was almost imperceptible compared to that of steel, even supported by electromagnetic field which allowed

$P–PO_4$ and total phosphorus reduction as small as 7% and 15.5%, respectively, in domestic sewage. Higher effectiveness was obtained for wastes made of powdered milk. Similarly low aluminium concentration in the wastewater treated proved that aluminium leaching was slow.

In a periodic system, aluminium is an active metal which can indicate that its corrosion is possible and fast. However, in aqueous solutions aluminium is passive [14]. In the presence of dissolved oxygen, aluminium is covered with a passive layer of aluminium oxide, although aerobic conditions are not responsible for the species passivity. In water with chlorides, pitting corrosion of aluminium is observed as a result of passive layer damage. However, the other anions present in the solution (e.g. nitrate, acetate, sulphate) can inhibit the corrosion. The oxide layer responsible for aluminium passivity is stable at pH ranging from 4.5 to 7 [15].

In aqueous solutions, iron corrosion mainly depends on the content of oxygen that has access to the metal surface [16], [17]. At low concentration of dissolved oxygen in water, iron ions pass into the solution in the form of Fe^{2+}, therefore the loss of anode metal is observed. In an available literature, the stages of a electrochemical reaction of iron leaching in water are not explained in the same way. A direct reaction involving anode was questioned. The reaction $Fe_m \rightarrow Fe^{2+}_{sol} + 2e$ was considered to be improper because of a high influence of pH on the kinetics of iron ionisation on anode. A great number of new theories and mathematical models describe the mechanisms and kinetics of electrochemical iron leaching in aqueous solution. Their authors emphasize that the rate of metal ion leaching depends on many different factors, e.g. pH, current intensity or oxygen concentration [16].

Single physical methods that have been used to improve the effectiveness of phosphorus removal from solutions are associated with a lot of exploitation difficulties. High exploitation costs and rather poor efficiency are considered to be the most common problems concerning electrodialysis or reverse osmosis [1], [3]. EMF applied as an additional element in wastewater treatment allows us to obtain highly positive effects. As a single physical element it reduces the concentration of pollutants, and used simultaneously with metal packing it is more effective in wastewater treatment.

Coagulation induced by EMF may have influenced positively the removal of $P–PO_4$. It has been proved that this physical factor modifies the electrokinetic potential and influences the coagulation process [18]. EMF affects physicochemical characteristics of municipal sewage. It has been revealed that the time of complete sedimentation in the wastewater exposed to EMF was considerably shorter than that in the system without magnetic activation [10]. The suspended solid removal could be responsible for COD removal as well.

It was shown that EMF efficiently reduced the content of organic carbon compounds. The most effective proved to be the system combining the steel packing with physical factor. Solutions exposed to EMF are characterized, among others, by reduced surface tension and in contact with the atmosphere they adsorb paramagnetic particles of oxygen [10], [19]. High concentration of molecular oxygen in the wastewater analysed may have accelerated the processes of degradation of organic matter, all the more because the compounds resistant to degradation were absent.

Most microorganisms that are able to degrade organic compounds belong to aerobes. Thus, in the liquids exposed to EMF, with an increased oxygen concentration, they grow more abundantly, hence the degradation of organic matter is more efficient [20], [21]. A relatively long retention time in the technological system, i.e. 48 hours in the second phase, may have positively stimulated the growth of some microorganisms. It seems that the proliferating bacterial biomass may have degraded organic matter present in the wastewater exposed to EMF. This fact has been confirmed by the laboratory studies of biodegradation of organic compounds introduced in the area exposed to EMF. It was revealed that within the induction range of 0.005–0.14 T magnetic field promotes biodegradation processes in activated sludge. It was also confirmed that magnetic field affects the degradation of organic compounds for about 12 hours after completion of its effect [9], [10].

Another phenomenon which may occur under the impact of magnetic field is the intensification of free radicals' formation [22], [23]. High reactivity and high oxidation potential of those compounds may effectively have reduced the concentration of organic matter contained in the liquids investigated [23]. Disintegration of a water molecule with formation of free radicals takes place when a sufficient amount of energy is available. This can be induced by magnetic field. Free radicals have one or more unpaired electrons which explains their extreme reactivity. Through the intersystem crossing they often assume the configuration which stimulates formation of bonds between the radicals. However, this process can be hindered by relatively weak magnetic field which reduces the number of radicals that assume the single configuration, with a parallel preservation or increase of their total number [24].

The impact of the magnetic field on the reaction rate and the amount of generated $OH^{\bullet}$·radicals in the Fenton reaction was for the first time determined on the grounds of sodium sulphite (Na_2SO_3) concentration variations. After 120 minutes of the reaction, a 74% sulphite reduction was observed; with no magnetic field – the reduction reached only 25%. In the system modified by magnetic field, the oxidation rate r equalled –7.94 mg/dm^3·min, whereas in the case where only the reagents were applied the reaction rate amounted to merely –0.74 mg/dm^3 · min. This means that magnetic field increased the oxidation rate by over 10 times [23].

Leaching of metal ions had an influence on the reduction of organic carbon compounds, especially for steel packing. This phenomenon was due to a corrosion effect and suspension precipitation.

It is difficult to explain the processes that govern the wastewater treatment by this method. Corrosion is a very complex process and its mechanisms are not precisely known. Depending on process conditions, the corrosion effectiveness is different and for this reason the pollutant reduction is different as well.

5. CONCLUSION

- The metal packing in a technological system improves pollutant removal from wastewater.
- Of two types of metal packing used in a technological system, steel packing more effectively removes the pollutants than aluminum packing.
- Phenomena caused by electromagnetic field favourably influence the wastewater treatment.
- The efficiency of pollutant removal from domestic sewage and the wastes prepared from powdered milk was similar.
- Due to corrosion of steel packing there was observed a secondary pollution of wastewater with iron compounds.

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WPŁYW STAŁEGO POLA ELEKTROMAGNETYCZNEGO NA USUWANIE FOSFORU ZE ŚCIEKÓW W UKŁADACH Z WYPEŁNIENIEM METALOWYM

Przebadano możliwość wykorzystania stałego pola elektromagnetycznego (SPE) jako czynnika wpływającego na ograniczenie stężenia fosforu w ściekach oczyszczanych z zastosowaniem wypełnienia metalowego. Określono wpływ roztwarzanego metalu (Al, Fe) na skuteczność usunięcia związków fosforowych (P–PO_4, $P_{og.}$) i węglowych (ChZT) oraz wpływ SPE na zmniejszenie wartości tych wskaźników. Najwydajniejszy okazał się układ, w którym wykorzystano jednocześnie czynnik fizyczny i wypełnienie stalowe. W tym przypadku 48 h czas zatrzymania pozwolił całkowicie usunąć P–PO_4 zarówno ze ścieków bytowo-gospodarczych, jak i spreparowanych z mleka w proszku. Ten wariant technologiczny był najskuteczniejszy również w przypadku ograniczania stężenia pozostałych analizowanych wskaźników. W zależności od czasu zatrzymania i rodzaju ścieków sprawność usunięcia $P_{og.}$ wynosiła 38%–98%, a wartość ChZT została ograniczona o 10%–63%.