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Effect of Sludge Conditioning by Chemical Methods with Magnetic Field Application

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Abstract

The feasibility of magnetic field was examined as a factor affecting sludge conditioning intensification. In the experiment sludge after preliminary anaerobic digestion was used, coming from a domestic wastewater treatment plant. Digested sludge was taken directly from a fermentation tank. The experiment was run in three phases. They were performed on a laboratory scale, at various experimental stands. Different dosages of iron chloride, hydrogen peroxide and Fenton's reagent were applied to determine their influence on the sludge properties as well as the effect of constant magnetic field on the conditioning parameters was determined. Straight dependence was found between dosage of the reagents and the way of sludge introduction in the magnetic activity zone, as well as physical and chemical parameters of the prepared sludge.

Keywords: advanced oxidation process, Fenton reaction, magnetic field, sludge conditioning, sludge dewatering

Introduction

Operation of a wastewater treatment plant is closely related to the need for proper sludge management. Sludge generated in wastewater treatment processes must be subjected to processing and afterwards reused or disposed of. At present, there are practically no problems concerning carbon and nutrient removal from wastewater to be solved as the available technologies assure sufficient reduction [1]. Compared to the knowledge and technology of wastewater treatment, the sludge issue lags fairly behind. Despite the considerable progress observed in past years regarding the methods and technologies of sludge treatment, the question of effective neutralization remains open [2].

Needed most of all are modifications and changes to the currently practiced sludge conditioning methods, which will effectively decrease mass, remove organic substances susceptible to putrefaction, remove odour, improve dewatering parameters, and diminish the number of pathogenic organisms, all alongside economic use of the reacting chemicals [1, 2]. However, from the technological point of view, the main objective of sludge conditioning is to decrease specific filtration resistance, paying by increased dewatering effectiveness and sludge hydration reduction. Currently regarded as the best sludge conditioning method is the application of polyelectrolytes, which effectively reduces the repelling force between particles [3]. On the other hand, the present tendencies towards chemical agents reduction and process optimisation, prompt the search for new technologies of sludge preparation to dewatering, and to positively modify the other properties. An alternative to the now practiced methods may become the techniques used with much success in water and wastewater treatment, such as the efficient chemical methods based mainly on intensive oxidation of contaminants, supported with physical factors [4, 5, 6].

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In wastewater treatment methods are commonly applied in contaminant removal make use of advanced oxidation processes (AOP) or wet oxidation processes (WOP). One of the methods of AOP is the process that occurs while using hydrogen peroxide (H_2O_2) [7, 8, 9, 10]. It is an environment-friendly oxidant, commonly applied in wastewater treatment, as it is broken down to simply water and oxygen. H_2O_2 can react with pollutants directly or after preliminary ionisation or dissociation into free radicals ($OH^·$). The most frequently used catalyst is the redox system Fe(II)-Fe(III). Application of this catalyst in parallel with H_2O_2 is called the Fenton reaction. An effect of the catalytic break-down of H_2O_2 by ferrous or ferric ions, is the creation of high-reactivity $OH^•$, with high oxidizing potential of 2.8V [6, 11, 12, 13]. The Fenton reaction pathway is given as [13, 14]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^·$$

In order to improve treatment effect, activity of H_2O_2 is supported with ultraviolet radiation or gamma radiation [4, 15, 16]. However, application of these catalysts is often quite problematic. In the case of UV radiation, application of larger doses of H_2O_2 is necessary. Use of gamma radiation generates substantial operational difficulties and requires high-tech facilities. Therefore, more attention was paid to magnetic field as alternative to those methods [4].

Application of the advanced oxidation process (AOP) with Fenton's reagent, supported by magnetic field forces, has brought about very good results in industrial and sanitary wastewater treatment. Effectively removed from the wastewater were organic and phosphorus compounds and the sewage-like odour. Attention should be paid to the fact that the treatment processes occurred very fast, and the magnetic field introduction to the system resulted in substantial reduction of the applied doses of reacting substances [5, 6].

Effectiveness of Fenton reaction has been confirmed also in the case of sludge conditioning of domestic [17] and industrial origin [18]. This technique has enabled reduction of specific filtration resistance, increased the dewatering rate and dry weight of sludge. Simultaneous application of the chemical method and the electromagnetic field generated by AC, has efficiently improved the conditioning process and the properties of the sludge treated in this way [17].

The presented experiments reveal that the AOP may be widely applied in sludge preparation technology. They comprise a solid base for further research in the optimisation of this process and seeking factors increasing efficiency of this technology. The priority remains care for economic use of the reacting substances and introduction of elements promoting their limited use without compromising the technological effect.

It seems that the factor fulfilling the above condition is the magnetic field. Purposefulness of the constant magnetic field application has been justified in the case of water treatment [19, 20], wastewater treatment [5, 6, 21, 22] and sludge conditioning [17]. The technological and economic aspects of the discussed process prompt forcibly to test magnetisers as devices intensifying the AOP. Magnetic activators of liquids are characteristic of simplicity in construction and do not require any feeding source. Properly operated, they are able to sustain the value of magnetic field intensity for a long time. It has been evidenced that their application supports reduction of the quantity of reacting substances, at the same time preventing satisfactory technological effect, and in a positive way modifies the physico-chemical parameters of solutions [4, 6, 9, 21, 22].

The presented experiments were aimed to assess an unconventional method of sludge preparation by exposure to magnetic fields. They were conducted with regard to the field energy application in the conditioning processes based on individual activity of the physical factor or in associated systems with dosing of reacting chemicals.

Materials and Methods

In the experiments, sludge after preliminary anaerobic digestion was used, coming from a domestic wastewater treatment plant. Digested sludge (preliminary and surplus sludge mixed) was taken directly from the fermentation tank. The experiments were conducted in three phases, on various laboratory-scale examination stands at the ambient temperature of 20ºC.

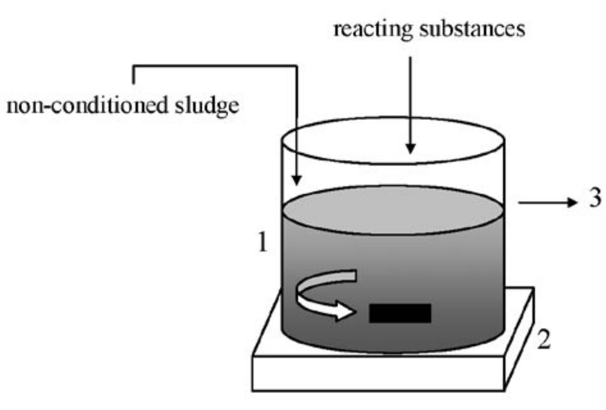
In phase I the importance and the efficiency of only the chemical additives in the sludge conditioning process were determined. Phases II and III were aimed to assign the quality of the direct impact of magnetic field on the conditioning and to determine its influence on the sludge parameters when treated with the applied reagents. The last two phases differed in the way of sludge introduction in the magnetic field exposure zone.

Depending on the series of the experiment, the system was introduced with either Fe(III) ions as $FeCl_3 \cdot 6H_2O$, H_2O_2 as 30% perhydrol dilution, or Fenton's reagent (Fe(III) and H_2O_2). In the case of Fenton's reagent, the reactor was first added with the iron ions, and directly after with H_2O_2. The applied doses of the reacting substances are shown in Table 1.

Sludge detention time in the system was 24 h. Samples for the physico-chemical analyses were taken directly from the reactors, right after termination of the experiment.

Table 1. Doses of the reacting substances applied in the experiment.

Dose	Fe(III) [g/dm^3]	H_2O_2 [g/dm^3]	Fenton's reagent [g Fe(III)/dm^3]	[g H_2O_2/dm^3]
1	0.30	1.00	0.30	1.00
2	0.60	2.00	0.60	1.00
3	1.00	4.00	1.00	4.00



1. container with sludge; 2. magnetic stirrer; 3. sludge after conditioning.

Fig. 1. Scheme of the experimental stand in phase I.

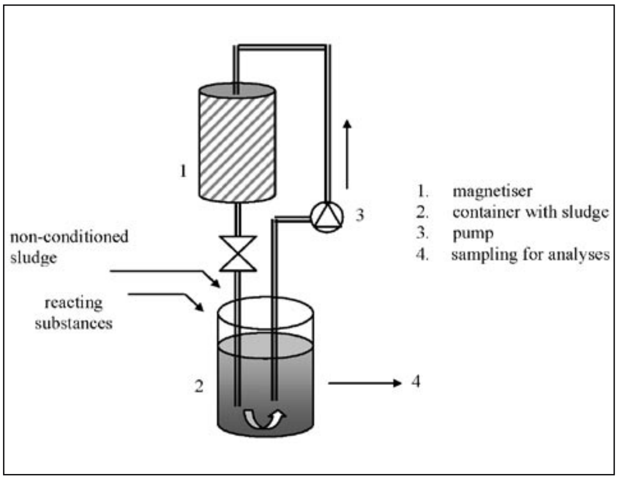


Fig. 2. Experimental stand in phase II (dynamic method).

In phase I, a laboratory reactor of 1 dm^3 volume was used, equipped with a magnetic stirrer (Fig. 1). At the start of a cycle, right after addition of the reacting substances, sludge was mixed 15 minutes at 200 rpm in order to distribute evenly the reacting substances in the reactor. Afterwards, the sludge was kept immobile in the reactor.

Examinations of phase II were conducted with the help of a device for magnetic activation of liquids. The magnetiser consisted of a steel, cylindrical body and a magnetic pile. The magnetic pile was made of permanent magnets generating constant magnetic induction field of an intensity range: 0.4 – 0.6 T (Fig. 2). Sludge was contained in a 1 dm^3 container and fed to the magnetiser by membrane pump of 0.5 dm^3/min. delivery (Fig. 2). In this phase of the experiment mixing was executed due to wastewater flow through the system and thus the magnetic stirrer wasn't used. In this phase we additionally determined the influence of sludge pumping on its physico-chemical parameters. It was executed by sludge pumping (with no conditioning factors applied) with a membrane pump of 0.5 dm^3/min. delivery for 24 h.

In phase III, 1.0 dm^3 of sludge was added with precisely determined doses of the reacting substances, thoroughly mixed with magnetic stirrer for 15 min. and the whole contents exposed to the magnetic field. The sludge was kept immobile in the magnetic field for 24 h. The magnetic reactor comprised a 3.0 dm^3 magnetiser, with the following dimensions:

total length: L = 170 mm

nominal diameter of the tube: D = 150 mm.

In all series sludge susceptibility to dewatering through measuring the time of vacuum filtration, specific filtration resistance, and final hydration of the sludge cake were determined [23]. Composition of the sludge was analyzed through dry weight, mineral residue and volatile substances determinations (PN – 75/C – 04616.01). In the filtration effluent the content of organic substances expressed as COD with dichromate as the oxidizing agent (PN – 74/C – 04578) was determined. Residual, unused H_2O_2 in the filtration effluent was not taken into consideration during COD determination.

The conditioned sludge quality was compared to the quality of the sludge which had not been treated with any conditioning agents.

Results

The physico-chemical parameters of the anaerobically digested sludge are presented in Table 2.

Results of the first phase enabled a comparison of the effectiveness of the individual conditioning agents and their impact on the sludge properties after 24-hour reaction time. The most efficient reacting substance was Fenton's reagent, which modified the prepared sludge in the most distinct way (Tab. 3, Fig. 4, Fig. 5). The system's introduction with a coagulant ($FeCl_3$) and strong oxidising agents (H_2O_2 and Fenton reagent) improved considerably all the analyzed values. Especially important is the decrease of sludge dewatering time on the vacuum filter and reduction of the specific filtration resistance value to $0.455 \cdot 10^{13}$ m/kg, at the highest dose of Fenton's reagent applied (Fig. 4, Fig. 6). The final effect of the conditioning was improving along with the addition of higher doses of the regents. The Fenton reaction resulted in the decrease of organic substance concentration in the sludge, and COD in the effluent from the vacuum filter (Tab. 3, Fig. 5, Fig. 7). The amounts of volatile substances, depending on the applied dose of the Fenton reagent, were contained in the range between: 12.988 g/dm^3 and 12.142 g/dm^3, whereas COD concentration in the effluent varied from 689.50 mgO_2/dm^3 to 420.65 mgO_2/dm^3.

Application of only $FeCl_3 \cdot 6H_2O$ in the conditioning process also resulted in a positive modification of the sludge properties. However, filtration rate, specific resistance (Fig. 8) and other indicator values of the sludge prepared only with iron salts vary considerably from those obtained when the Fenton reagent was added to the system (Fig. 4, Fig. 5). This was especially visible at

Table 2. Physico-chemical parameters of the anaerobically digested sludge, and the sludge after 24-hour pumping.

Sludge parameters	Anaerobically digested sludge	Anaerobically digested sludge after 24-hour pumping
filtration time [sec]	4000	12000
specific filtration resistance [m/kg]	$7.700 \cdot 10^{13}$	$13.931 \cdot 10^{13}$
sludge cake hydration after filtration [%]	93.1	92.25
dry weight [g/dm^3]	32.052	31.940
mineral residue [g/dm^3]	14.824	14.96
volatile substances [g/dm^3]	17.228	16.980
effluent COD [mg O_2/dm^3]	750.00	1175.50

Table 3. Physico-chemical parameters of the anaerobically digested sludge after 24-hour conditioning with the chemical additives – phase I.

Sludge parameters after conditioning	Dose of Fe(III) [g/dm^3]			Dose of H_2O_2 [g/dm^3]			Dose of Fenton's reagents [gFe(III)/dm^3] [mg H_2O_2/dm^3]		
	0.30	0.60	1.00	1.0	2.0	4.0	0.30 1.0	0.60 2.0	1.0 4.0
filtration time [sec]	490	390	220	3000	2520	2340	260	240	195
specific filtration resistance [m/kg]	$0.979 \cdot 10^{13}$	$0.873 \cdot 10^{13}$	$0.555 \cdot 10^{13}$	$6.856 \cdot 10^{13}$	$3.917\ 10^{13}$	$2.317 \cdot 10^{13}$	$0.656 \cdot 10^{13}$	$0.586 \cdot 10^{13}$	$0.455 \cdot 10^{13}$
sludge cake hydration after filtration [%]	87.44	87.21	84.92	89.50	89.40	87.13	89.11	88.95	86.21
dry weight [g/dm^3]	34.167	35.005	35.784	33.951	33.754	32.901	34.479	34.097	34.712
mineral residue [g/dm^3]	19.933	20.355	21.033	17.74	16.831	17.694	21.491	21.19	22.57
volatile substances [g/dm^3]	14.234	14.650	14.751	16.211	16.923	15.207	12.988	12.907	12.142
effluent COD [mg O_2/dm^3]	642.00	591.14	485.0	740.19	750.53	810.67	689.50	507.3	420.65

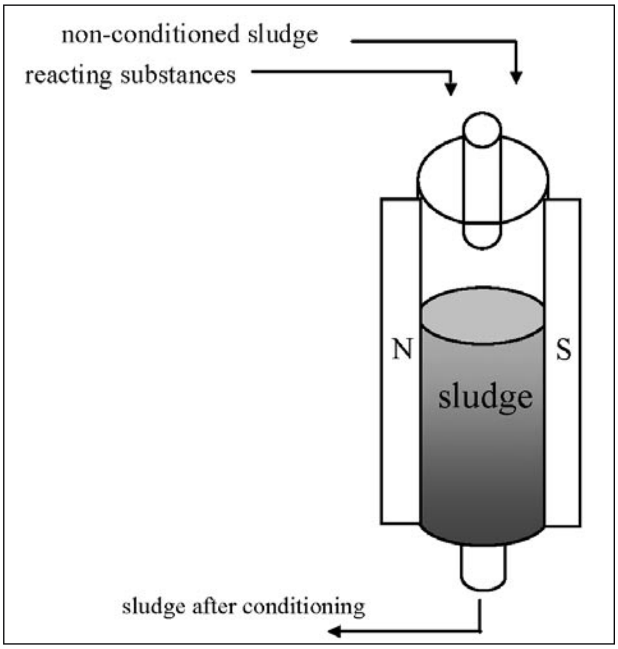


Fig. 3. Experimental stand in phase III (static method).

low doses of the reacting substances (Tab. 3). Dewatering time at the lowest dose of iron chloride applied reached 490 sec., whereas the lowest dose of Fenton's reagent decreased this value to 260 sec. Likewise, application of the coagulant only, was a less efficient way to reduce COD in the anaerobically digested sludge (Tab. 3). The least effective conditioning agent appeared to be hydrogen peroxide. Application of the highest dose of H_2O_2 decrease the filtration time to 2340 sec., and the specific filtration resistance value to $2.317 \cdot 10^{13}$ m/kg (Tab 3, Fig. 4). These results exceed a few times those obtained while conditioning with iron chloride or Fenton's reagent. The use of hydrogen peroxide alone only slightly modified the sludge composition and resulted in lower hydration of the sludge cake after filtration, as compared to the non-conditioned sludge. High doses of H_2O_2 resulted in the COD increase in the effluent (Tab. 3, Fig. 5). Application of H_2O_2 as the only conditioning agent resulted in complete odour removal in the conditioned sludge, Fenton's reagent obtained the same technological effect.

Phase II of the experiment was aimed at studying the effect of sludge conditioning using magnetic field forces.

In this phase the non-conditioned sludge and the sludge with the chemical additives were fed to the magnetiser with a membrane pump (delivery 0.5 dm^3/min.). Sludge pumping through the magnetic activity zone did not improve the physico-chemical parameters. It has been revealed that the applied technique of sludge introduction in the zone of the physical factor activity causes considerable deterioration of all analyzed indicators (Tab. 4, Fig. 4, Fig. 5). Time of sludge dewatering that was not mixed with any reacting substances and subjected to 24-hour pumping through the magnetic activator of liquids was extended two times in comparison with the non-conditioned sludge. The effluent COD also increased considerably and amounted to 922.01 mg O_2/dm^3. Parallel use of the chemical reagents and magnetic field for the sludge conditioning did not have any positive effects, either. In all cases, sludge pumping through the magnetic activity zone was deteriorating the final effect of conditioning, as compared with the sludge preparation with only the reacting substances. The most distinct deterioration regarded the following parameters: time of vacuum filtration, specific filtration resistance, and effluent COD (Tab. 4, Fig. 4, Fig. 5). Application of $FeCl_3 \cdot 6H_2O$ in this technological system stimulated the filtration time limitation to the range of 2730-580 sec., depending on the applied coagulant dose. The values are a few times higher than those obtained in the system without magnetic field. Similar relations can be noted for specific filtration resistance or COD (Fig. 8, Fig. 9). Sludge pumping through the magnetic activity zone negatively affected the sludge conditioning in a smaller degree when the advanced oxidation method was used. Although sludge properties deterioration was also observed in this case, the final effect was not so evident as in the case of iron chloride (Fig. 6, Fig. 7). The physico-chemical method of sludge treatment had a smaller effect on the modification of dry weight, volatile substance concentration, or mineral residue in the case of all chemical additives.

Since the obtained results of the sludge preparation in magnetic field were much worse than expected, we investigated. Additional series of the experiments was carried out in order to determine the influence of pumping on the sludge structure and properties. It has been evidenced that the delivery rate of 0.5 dm^3/min. worsens sludge quality (Tab. 2). Dewatering time in an experimental vacuum filter amounted up to 12,000 sec., and COD in the effluent equalled 1175.5 mgO_2/dm^3. These were the worst values of the physico-chemical parameters of the conditioned sludge. The data have revealed that a too high delivery rate autonomously destroys the sludge structure and deteriorates the final results of the conditioning process. Therefore, it has been concluded that in order to improve the effect of magnetic field activity, sludge must be introduced in the magnetic activity zone in a less dynamic way.

In phase III the sludge, after mixing with chemical reagents, was fed to the magnetic reactor in one batch and left out for 24 hours to react. In this series of the experiment the sludge subjected to magnetic field activity was immobile. The applied method comprising parallel chemical conditioning and physical forces has brought about some very positive results. Changes in the properties of prepared sludge regarded mainly organic compounds (Fig. 5). Especially markedly the magnetic field modified the parameters of sludge conditioned with Fenton's reagent (Tab. 5). Reduced were the contents of volatile substances in the sludge and COD in the effluent. The concentration of the volatile substances in the sludge ranged from 12.574 g/dm^3 to 11.817 g/dm^3, COD in the effluent from 550.20 mgO_2/dm^3 to 300.15 mgO_2/dm^3, depending on the applied dose of the reagents (Tab. 5, Fig. 7). The parameters characterising sludge susceptibility to dewatering did not change considerably in comparison with phase II: magnetic field introduction lowered the filtration time to 190-270 sec., and the specific filtration resistance to $0.421 \cdot 10^{13}$ - $0.727 \cdot 10^{13}$ m/kg (Fig. 6). Application of hydrogen peroxide as the only conditioning agent and magnetic field had no visible effects. Only the COD and volatile substances concentration in the effluent were slightly reduced (Tab. 5, Fig. 5). COD concentration compared with the system without the physical factor and at the highest dose of perhydrol it amounted to 740.70 mg O_2/dm^3. Magnetic field did not play an important role in the sludge conditioning with only iron chloride. Neither the susceptibility to dewatering, nor the composition of sludge changed markedly after introduction of the physical factor to the system (Tab. 5, Fig. 8, Fig. 9).

Discussion

The aim of the presented study was to determine the impact of constant magnetic field on various conditioning methods of a sludge after preliminary anaerobic digestion. Compared was the importance of the physical factor in the classical method with $FeCl_3 \cdot 6H_2O$, in the method with hydrogen peroxide, and in the advanced oxidation method with Fenton's reagent.

For most applications, it does not matter whether Fe^{2+} or Fe^{3+} salts are used to catalyze the reaction. The catalytic cycle begins quickly if H_2O_2 and organic material are in abundance. However, if low doses of Fenton's reagent are being used (e.g., < 10-25 mg/L H_2O_2), some research suggests ferrous iron may be preferred [13, 24, 25]. Neither does it matter whether a chloride or sulfate salt of the iron is used, although with the former, chlorine may be generated at high rates of application [13].

Because Fe^{3+} have better coagulation properties it was used in the experiment. This fact has an essential, positive influence as for size reduction molecules of sludge flocculation and agglomeration. It causes the increase in effectiveness dewatering and the decrease in sludge hydration. This kind of catalyst led to better phosphorus and organic compounds reduction in the filtrate, which seems to be significant in neutralization of the water after filtration. The application of Fenton reaction with ferric iron as a catalyst is commonly used and technological effects

Table 4. Physico-chemical parameters of the anaerobically digested sludge after 24-hour conditioning by sludge pumping through magnetic activity zone (dynamic method) – phase II.

Sludge parameters	Magnetic field	Magnetic field Dose of Fe(III) [g/dm^3]			Magnetic field Dose of H_2O_2 [g/dm^3]			Magnetic field Dose of Fenton's reagents [gFe(III)/dm^3] [mgH_2O_2/dm^3]		
		0.30	0.60	1.00	1.0	2.0	4.0	0.30 1.0	0.60 2.0	1.0 4.0
filtration time [sec]	11000	2730	1620	580	4220	3870	3640	590	551	425
specific filtration resistance [m/kg]	$11.342 \cdot 10^{13}$	$3.995 \cdot 10^{13}$	$2.113 \cdot 10^{13}$	$0.988 \cdot 10^{13}$	$7.790 \cdot 10^{13}$	$7.230 \cdot 10^{13}$	$6.900 \cdot 10^{13}$	$0.882 \cdot 10^{13}$	$0.861 \cdot 10^{13}$	$0.860 \cdot 10^{13}$
sludge cake hydration after filtration [%]	91.33	91.67	90.17	91.10	89.52	90.64	89.45	88.81	88.90	88.39
dry weight [g/dm^3]	33.119	32.901	33.132	33.021	33.465	33.386	33.576	34.071	34.213	34.709
mineral residue [g/dm^3]	19.879	19.000	19.918	19.850	18.222	18.176	17.732	21.691	21.223	22.239
volatile substances [g/dm^3]	13.240	13.901	13.214	13.171	15.243	15.210	15.844	12.380	12.990	12.470
effluent COD [mg O_2/dm^3]	922.01	730.70	724.12	710.89	792.18	772.98	790.00	691.5	674.91	632.0

Table 5. Physico-chemical parameters of the anaerobically digested sludge after 24-hour conditioning by detention in the magnetic reactor (static method) – phase III.

Sludge parameters	Magnetic field	Magnetic field Dose of Fe(III) [g/dm^3]			Magnetic field Dose of H_2O_2 [g/dm^3]			Magnetic field Dose of Fenton's reagents [gFe(III)/dm^3] [mgH_2O_2/dm^3]		
		0.30	0.60	1.0	1.0	2.0	4.0	0.30 1.0	0.60 2.0	1.0 4.0
filtration time [sec]	3700	490	370	230	3050	2730	2530	270	240	190
specific filtration resistance [m/kg]	$7.253 \cdot 10^{13}$	$0.984 \cdot 10^{13}$	$0.869 \cdot 10^{13}$	$0.721 \cdot 10^{13}$	$6.813 \cdot 10^{13}$	$3.876 \cdot 10^{13}$	$3.294 \cdot 10^{13}$	$0.727 \cdot 10^{13}$	$0.613 \cdot 10^{13}$	$0.421 \cdot 10^{13}$
sludge cake hydration after filtration [%]	90.50	88.21	87.50	84.34	89.90	90.20	89.87	88.57	88.25	85.87
dry weight [g/dm^3]	32.450	33.904	34.430	35.500	33.306	33.002	32.951	34.924	34.812	35.748
mineral residue [g/dm^3]	18.043	19.990	20.901	21.629	18.431	19.605	18.983	22.350	22.421	23.931
volatile substances [g/dm^3]	14.407	13.914	13.529	13.871	14.875	13.397	13.968	12.574	12.391	11.817
effluent COD [mg O_2/dm^3]	730.0	640.40	585.50	490.60	690.45	735.85	740.70	550.20	420.35	300.15

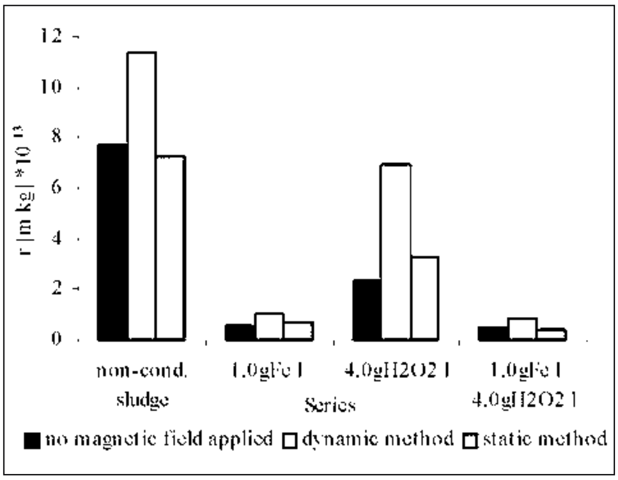


Fig. 4. Magnetic field impact on the specific filtration resistance, at the highest doses of reacting substances.

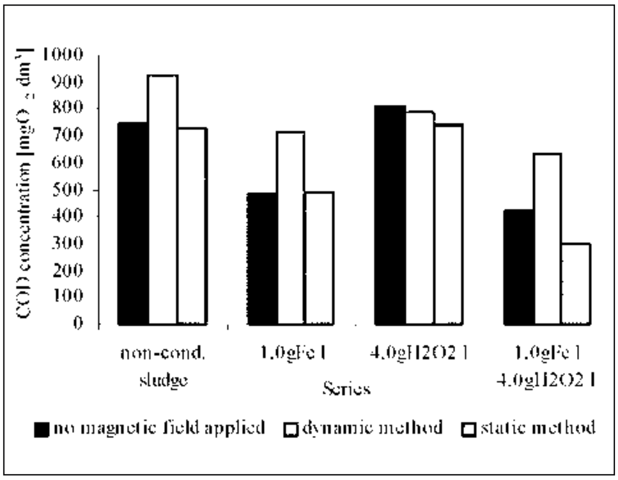


Fig. 5. Magnetic field impact on COD, at the highest doses of reacting substances.

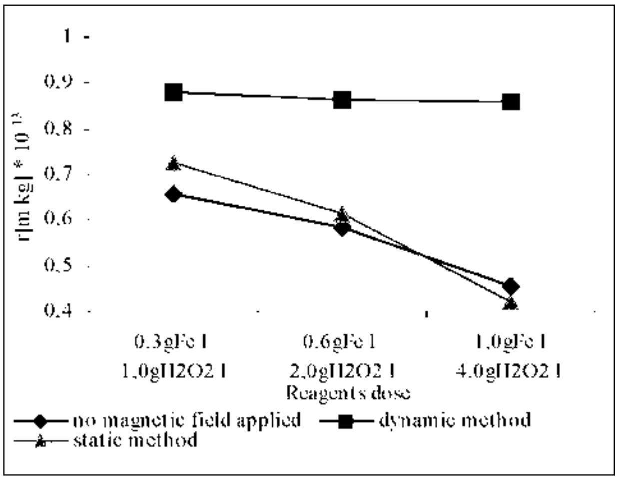


Fig. 6. Fenton's reagent impact on specific filtration resistance.

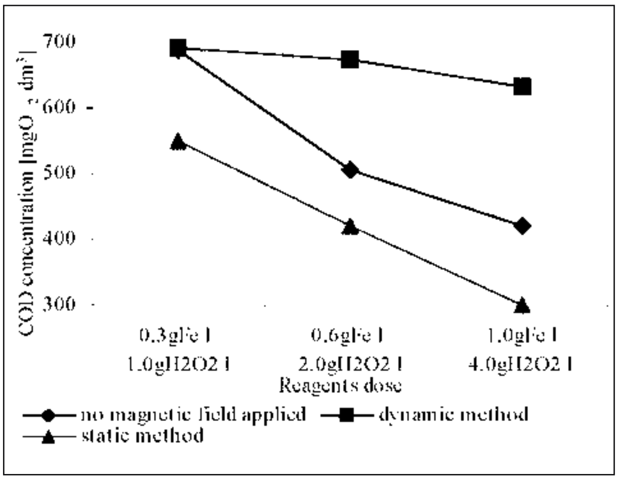


Fig. 7. Fenton's reagent impact on COD.

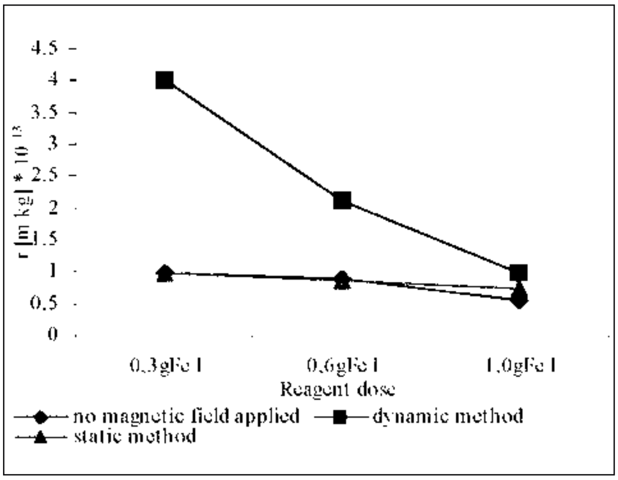


Fig. 8. Iron chloride impact on specific filtration resistance.

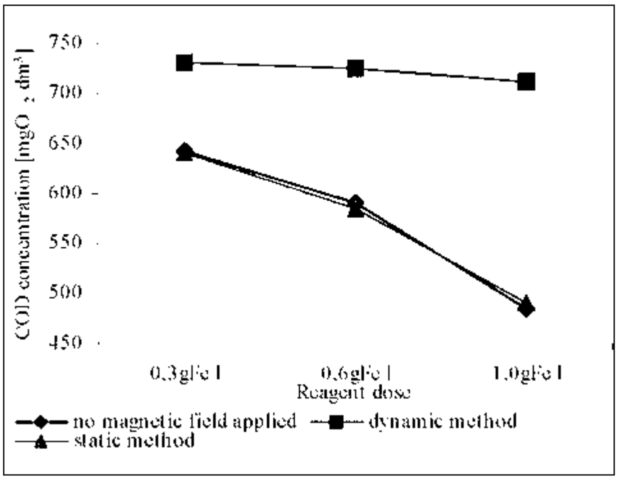


Fig. 9. Iron chloride impact on COD.

are as effective as for the classically generate free radicals reaction [26]. The mechanism of Fenton reaction pathway is given as [14]:

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\cdot} + Fe^{2+} + H^+$$
$$HO_2^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2$$

and next classical Fenton reaction:

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\cdot} + Fe^{3+} + OH^-$$

Generally, when the Fe^{2+} salts are used, radicals $OH^{\cdot}$ are generating immediately throughout reaction between Fe^{2+} ions and H_2O_2. When the Fe^{3+} salts are used radicals $OH^{\cdot}$ are generating in a two-stage process throughout slow reaction between Fe^{3+} ions and H_2O_2, next quick reaction between Fe^{2+} ions and H_2O_2 [27].

In phase I, with no magnetic field applied, the most effective conditioning agent was Fenton's reagent. Its efficiency was displayed by reducing of the specific filtration resistance, the final hydration of the sludge cake and the COD concentration in the effluent. It seems that the positive effect of sludge preparation by advanced oxidation method is directly related to the coagulating properties of iron chloride and the oxidising force of the free radicals formed in this reaction. Application of such combination of chemical substances diminished the content of organic compounds in the sludge and in the effluent, and resulted in coagulation of fine particles of the sludge. The presented properties of Fenton's reagent were used in both wastewater treatment [5, 6, 28] and sludge preparation [17, 18]. The experiments used a heavily contaminated sludge from a treatment plant of chemical industry effluents. The obtained results of sludge digestion with the application of Fenton reaction were more efficient than in the classical method of aerobic digestion. The experiments resulted in the reduction of the organic substances resistant to degradation by about 50%, and thus to the reduction of the volume of the digested sludge. Also observed was the positive impact of Fenton reaction on the susceptibility to dewatering of the digested sludge. Time of the capillary suction was reduced by a few times in comparison to raw sludge [18].

Use of hydrogen peroxide alone in the conditioning process had no visible effect on the physico-chemical parameters of the conditioned sludge. The most distinct changes were observed regarding shorter time of dewatering and reduction of specific filtration resistance, although the results obtained while using this reagent were incomparably worse in spite of applying Fenton's reagent or iron chloride. Practically no organic matter (determined as COD) reduction was observed in the effluent, and in the case of higher doses of hydrogen peroxide the value of this parameter was increasing. It might have been caused by the presence of residual H_2O_2 unused in the oxidation process. This reagent may be in contact with some oxidising agents which act as a reducer. Such phenomenon occurs e.g. in the case of reagent used for COD determination, i.e. potassium dichromate [29, 30]. It seems that when using high doses of H_2O_2 one mustn't forget to take into account the eventual content of residual H_2O_2 or to fully break down the remaining hydrogen peroxide. In the case when a solution contains residual H_2O_2, the COD value must be corrected in accordance with the rule incorporating the amount of this oxidant in the calculations of the actual COD value. Concentration of organic matter may be calculated from the following equation:

$$COD\ [mg/dm^3] = COD_m - c \cdot f$$

COD_m – content of organic matter determined by dichromate method [mgO_2/dm^3]
c - concentration of residual H_2O_2 [mg/dm^3], determined by e.g. iodimetric method
f – conversion factor 0,25 for residual concentration of H_2O_2 in the range of 20-1000 [mg/dm^3]

The obtained results of anaerobically stabilized sludge conditioning with only hydrogen peroxide have been confirmed by other experiments [29]. Sludge stabilisation with this oxidant for 21 days revealed an important increase of organic substance concentration, determined as COD, and considerably extended the capillary suction time. The COD value in the present experiment was only slightly lowered on the first day of stabilisation, and then rapidly increased, probably as a result of periodical deficiency of aerobic conditions. In this case, a much more effective appeared to be the classical aerobic stabilisation method, making use of compressed air as the oxidising medium [29].

H_2O_2 application as the only conditioning agent resulted in total extinction of bad odour of the conditioned sludge. American experiments confirm hydrogen peroxide use for reduction of bad odour of the sludge caused by H_2S. Application of perhydrol was a very effective and cheap solution. Comparisons have been made to the impact of the other popular strong oxidant $KMnO_4$, on the H_2S concentration in the sludge. The obtained results point indisputably at a much higher effectiveness of perhydrol. At similar concentrations of an oxidising agent, H_2O_2 reduced H_2S by 87-99%, whereas $KMnO_4$ by merely 38-68%. The following property in favour of perhydrol application is the much lower price. The described method was put into practice with full success at the wastewater treatment plant in Orlando, Florida [13].

Introduction to the system of the method comprising the conditioned sludge introduction into magnetic field with a pump of 0.5 dm^3/min. delivery had no positive effects. Reference data would suggest that magnetic field supports reduction of the surface tension and thus enables introduction of numerous oxygen particles to the sludge mass [21, 22]. This phenomenon should influence positively the biodegradation process and limit the concentration of organic substances in the sludge and the COD value in the effluent. A confirmed effect of water and wastewater magnetic preparation is the modification of the contained gases concentration. Magnetisation of tap water allows it to achieve full oxygenation capacity. Likewise, in the municipal sewage such treatment causes considerable increases in oxygen concentration. Magnetised solutions are characterized by the diminished surface tension and in contact with the atmosphere they adsorb the paramagnetic particles of oxygen. That's why their concentration in water solutions increases [22]. High concentration of the molecular oxygen in the analyzed sludge causes an increase in organic matter degradation, especially because the compounds resistant to degradation were absent in that case. Likewise, it was evidenced that magnetic activation of liquid and gaseous fuels allows for selective oxygen saturation of the fuel mixture in the unrestricted flow zone. Therefore, the combustion conditions for such a mixture are nearly optimal, which can be proven by a radical reduction of toxic substances in exhaust gases and more economic fuel consumption [22].

It has been also evidenced that it is possible to initiate the coagulation process in water solutions without chemical substance application, but only with the use of magnetic field forces. Studies of the magnetic treatment influence on the physico-chemical properties of municipal sewage have revealed that the settlement time of sewage prepared with magnetic field decreased considerably in comparison to the settlement time of non-prepared sewage. Additionally, a tendency was detected to coagulate fine particles of sludge in the magnetically prepared sewage, which eventually accelerates sedimentation and increases dewatering susceptibility [21]. However, it has also been evidenced that the properties of sludge prepared with this technique vary distinctly from those observed during conditioning without the physical factor application: the sludge susceptibility to dewatering deteriorated considerably. One of the analyzed parameters determining sludge susceptibility to dewatering is specific filtration resistance. Filtration resistance decreases along with an increase of the size of sludge particles. When particle size increases, the cross-section of pores increases and the specific surface diminishes, which in effect decreases the hydraulic resistance of the SS liquid phase in the sludge layer [31]. It may be concluded that every occurrence resulting in an increase of SS particle size will decrease filtration resistance. It appears that the same may be achieved through introduction to the system of chemical additives or treatment with properly shaped physical factors. Forces promoting agglomeration of single particles depend on their size, temperature, medium viscosity, pH, the applied chemical additive, and time and rate of slow and rapid agitation. Application in the second phase of the experiment of the 24-hour sludge pumping through the magnetic field exposure zone field obviously prevented creation of large and consistent flocs, which reduce dewatering time and the value of filtration resistance. It seems that the too high delivery of the sludge feeding pump has greatly increased the dispersion of the system and thus negatively influenced the sludge dewatering properties. Only application of the highest doses of the chemical additives resulted in relatively efficient dewatering in the experimental vacuum filter. Dispersed particles of the conditioned sludge were obviously transferred to the effluent and increased the concentration of organic matter. In this phase of the experiment the effluent COD was very high, even with the application of iron chloride or Fenton's reagent.

In previous studies of wastewater sludge no attempts have been made to use an electromagnetic field to improve Fenton reaction conditions and to intensify the process of hydroxyl radicals creation. The latter are created in the processes of homolytic disruption of bounds or as a result of electron transfer between particles of chemical compounds. Free radicals have one or more non-bonding electrons. Through intersystem crossing they can enter a configuration that enables creation of bounds between free radicals. The intersystem crossing can be inhibited by relatively weak electromagnetic fields. This results in reduction of the intersystem crossing efficiency, which in turn decreases the number of radicals transformed into singlet configuration with parallel preservation or rise of their total number. Therefore, magnetic fields are regarded as factors able to generate free radicals [5, 6]. This relation was successfully used in phase III of the experiment. A magnetic reactor was used with immobile sludge inside, prepared in advance with chemical additives. The applied technological system clearly improved the sludge properties after treatment with Fenton's reagent, and in a smaller degree with hydrogen peroxide. It regarded mainly the reduction of organic matter in the sludge and COD in the effluent. It was observed that a properly shaped electromagnetic field has an impact on the performance of the outer electronic shell in water particles and in the substances dissolved in this water, but also on the activation of valence electrons. Magnetic field influences the changes of electronic spins direction in atoms, on the rate of internal conversion of free radicals couples, and on the relaxation mechanisms, but also on the fission of electronic energy levels and atomic nuclei [6, 21].

Such types of exposure to a magnetic field had no visible effect on the characteristics of the sludge treated with iron chloride. Previous studies have shown that application of an electromagnetic field proves feasible in wastewater treatment technology [5, 6] and should have very positive results in sludge preparation processes. They will not only result from the oxidising properties of the Fenton reaction product but also from the impact on sludge of the magnetic field alone. It has been proven that in certain conditions the active electromagnetic field can considerably influence reduction of sludge hydration and improve sludge dewatering parameters [32, 33]. Experiments conducted with the use of sludge prepared by the electromagnetic field alone, resulted in a hydration decrease from 94.5% to 85%, while the most effective appeared a 2–min. field activity. Satisfactory results were also obtained during examinations of specific filtration resistance. It has been found that properly adjusted intensity and time of electromagnetic field activity has an effect on reduction of this parameter's value [33].

Satisfactory results were obtained in the case of advanced oxidation method application and electromagnetic field for sludge conditioning for a 24-h period. Electromagnetic field of a defined induction was generated by electric current flow with alternating intensity through metal medium. The effect of the sludge properties variation was achieved owing to the triple mechanism: oxidation by free radicals, stimulating activity of electromagnetic field, and coagulation with iron salts supported by corrosion of the metal medium [17].

Conclusions

- In the case when the chemical additives alone have been applied, the most effective method of sludge conditioning is the advanced oxidation method with Fenton's reagent, whereas the least effective is hydrogen peroxide added alone to the system.
- Conditioning effectiveness rises along with the increase of iron chloride and Fenton's reagent doses.
- A magnetic field can have a stimulating effect on sludge conditioning, given the proper technological conditions.
- Too intensive pumping of sludge destroys its structure and results in considerable deterioration of the susceptibility to dewatering and of other properties.
- The applied methods of sludge conditioning mainly impact the sludge dewatering properties and COD concentration in the effluent; the effect on the sludge composition is of minor importance.
- Research concerning the effect of sludge stabilization by advanced oxidation process (with Fenton's reagent) with magnetic field application will be continued (grant KBN No.4 T09D 037 23: The influence of Fenton's reagent in magnetic field on sludge quality parameters).

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