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THE EFFECT OF WASTE PHOSPHOGYPSUM ON THE DENITRIFICATION AND DESULFURICATION PROCESSES

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The effect of waste phosphogypsum obtained after phosphoric acid production from apatites and phosphorites, on the processes of denitrification and desulfurication taking place with the use of bacteria from the genera *Bacillus* and *Desulfotomaculum*, have been investigated.

It has been shown that the phosphogypsum concentrations used in the experiments were can serve as a sulphate source for the *Desulfotomaculum* bacteria. The phosphogypsum is not toxic towards the bacteria. The phosphogypsum has also been found to play the role of an electron acceptor in the processes of oxidation of simple organic substrates in the processes of bioreduction of nitrates or sulphates. In the optimum conditions of desulfurication in a medium containing the phosphogypsum, organic substrate and *Desulfotomaculum ruminis* bacteria, the degree of conversion is close to 90%, and a decrease of TOC reaches about 50%.

Key words: phosphogypsum, denitrification, desulfurication, sulphate reducing bacteria (SRB)

INTRODUCTION

Phosphogypsum is a waste product of the process in obtaining phosphoric acid from apatites and phosphorites by extraction with sulphuric acid. It is characterised by strongly acidic pH, and apart from calcium sulphate (~95%) it contains some amount of adsorbed phosphoric acid, organic contaminants and a small admixture of rare earth metals (mainly lanthanides) (Praca zbiorowa, 1958). In Poland there are almost 40 mln tons of this waste, aggressive towards the natural environment, at dumping grounds near Boleslawiec (Wizow), Gdansk and Police (Kowalski et al.).

Because of high and increasing demand for phosphoric acid and its derivatives (fertilisers and detergents), the amounts of this waste are expected to increase. In the chemical plant Police, the dumping grounds are filled with about 20 mln tons of this waste and this amount is expected to increase each year by about 2 mln tons. The hitherto used methods of utilisation of this waste, including conversion into cement,

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construction materials or sulphuric acid have been uneconomic, as required high investment costs. An interesting alternative are the microbiological methods based on phosphogypsum biodegradation and simultaneously utilising the organic matter e.g. from the wastes from agricultural and food industry (Gąsiorek et al. 1986).

Under anaerobic conditions sulphate reducing bacteria (SRB) cause phosphogypsum biotransformation to hydrogen sulphide, whereas the organic matter is oxidised to CO_2 or simple organic acids (Przytocka-Jusiak et al. 1995). Because of the possibility of biodegradation of many different organic substances in the presence of sulphate, SRB have been successfully used for reduction of ChZT in wastes (Domagała et al 1991, Domka et al. 2000, Barton 1995). The sulphides formed in the process of SO_4^{2-} - reduction may be subjected to oxidation by sulphur bacteria *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. In this process sulphur and sulphuric acid are formed ((Gąsiorek et al. 1983).

The methods of detoxication and biodegradation of all kinds of wastes have recently gained recognition because of the need to tackle chemical contamination of the waste dumping grounds threatening ecological equilibrium. This paper presents effect of the concentration of phosphogypsum being a waste product from processing of apatites and phosphorites from Morocco in the Police Chemical Plant, on the processes of denitrification and microbiological reduction of sulphates with the use of bacteria from the genera *Bacillus* and *Desulfotomaculum*.

MATERIALS AND METHODS

MICROORGANISMS

Bacteria from the genus *Bacillus* were isolated and identified according to the earlier given procedure ((Waligórska et al. 1992). The sulphate reducing bacteria from the genus *Desulfotomaculum* were isolated in a modified Starkey medium, according to the earlier described procedures (Domagała et al. 1992). The phosphogypsum studied was the waste from the Police Chemical Plant (sample collected on June 20th, 2000) processing raw materials from Morocco. Prior to the introduction into bioreactors, the samples were grounded and sieved (mesh size 0.315 mm).

KINETIC STUDY

The process of denitrification was conducted at 37^{o}C in closed and sterilised glass reactors of 90 cm^3 capacity, filled with a portion of 50 cm^3 of the medium supplemented with phosphogypsum tested. After pH adjustment to 7.5, the contents of the reactor was inoculated with 4% inoculum of pure bacteria culture collected at the logarithmic phase of growth. The medium was sterilised under the conditions: p = 0.5 MPa, T = 120^{o}C for 20 minutes. Because of acidity production in the reaction environment, every two hours pH was corrected to 7.5 value. Samples taken at certain time intervals were subjected to determination of nitrate (V) and nitrate (III) concentrations.

The results analysed and interpreted were mean values obtained from three measurements of NO_3^- (nitrate) and NO_2^- (nitrite) concentrations. They were referred to the results obtained for the reference samples without phosphogypsum.

MICROBIOLOGICAL DESULFURICATION

The process was conducted at 37°C under anaerobic conditions (helium) at pH 6.8 – 7.2, in tightly closed glass reactors filled with 50 cm^3 of the modified sulphate-free Starkey medium containing [g/dm^3]: $MgCl_2$ x $6H_2O$ = 1.65, NH_4Cl = 1.00, K_2HPO_4 = 5.00, $CaCl_2$ = 0.13, $Fe(NO_3)_3$ x $9H_2O$ = 0.515, sodium lactate 10.16. After addition of appropriate amount of phosphogypsum, the medium was deoxidised and inoculated with 4% volume of inoculum collected from culture being in the logarithmic phase of growth (after 24h). The reaction rate was determined as the degree of sulphate conversion to sulphide measured at certain time intervals. To measure the degree of this conversion, the system was blown with helium and the H_2S released was collected in absorber containing 0.1N cadmium acetate. The equipment used in the study and the media were sterilised for 20 minutes at 120°C.

Parallel experiments were conducted under the same conditions, but using the standard Starkey medium (without phosphogypsum) for obtaining reference samples. The results are averages of at least 3 measurements. TOC (total organic carbon) – the index describing the content of organic substance, was determined by the dichromate titration before and after the experiment (Standard Methods, 1992).

CHEMICAL ANALYSES

Concentrations of sulphates were determined by the weight method (Pol. Kom. Normalizacji i Miar), calcium – by the complexometric method (Standard Methods, 1992), phosphates - by the spectrophotometric method (Williams 1985), total iron and magnesium - by ASA (ELA Unicam SP 90A spectrophotometer).

Concentration of nitrates (V) were measured using the ion-selective electrode Detector, and concentration of nitrates (III) – using the spectrophotometric method (Beckman DU-640 spectrometer, wavelength λ = 520 nm).

Concentration of sulphides was determined by the iodometric method after precipitation of CdS (Williams 1985).

RESULTS AND DISCUSSION

The chemical composition of the phosphogypsum studied is given in Table 1. Knowing this composition we could choose the correct proportion between sulphate ions and organic carbon in the reaction mixture. The impact of phosphogypsum on the environment was studied on the example of two well-known processes of microbiological conversion involved in the cycles of nitrogen and sulphur. Fig. 1 illustrates the effect of the concentration of the phosphogypsum on the process of denitrification by genus *Bacillus.*

Table 1. Chemical composition of Morocco phosphogypsum

Component	Content [% w/w]
SO_4^{2-}	60.25
Ca^{2+}	22.39
PO_4^{3-}	1.60
Mg^{2+}	0.06
Fe total	0.04
Insoluble matter	0.70

Phosphogypsum solubility at 25°C = 2.81 g/dm^3

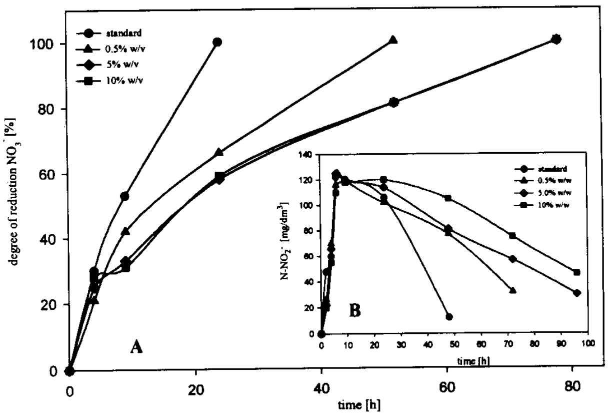
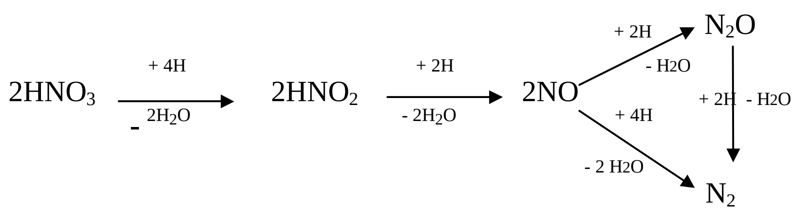


Fig. 1. The influence of the Marocco phosphogypsum concentration on efficiency of nitrates(V) reduction (A) and concentration of nitrates(III) (B) carried out in the presence of *Bacillus licheniforms* bacteria (pH = 7.5, T = 37°C, C/N = 2.28)

The kinetic curves of the process, obtained for three different concentrations of phosphogypsum in the medium and for the reference sample were similar, which indicated a similar mechanism of the process. No induction period of the reaction was observed. The presence of phosphogypsum causes only an extension of the time of the process. As the denitrification process studied involves the following intermediate compounds according to the scheme (Domka et al. 2000):



controlled the changes in the concentration of nitrates (III). As follows from the measurements of changes in NO_2^- concentration (Fig. 1b), the concentration of nitrates (III) at first strongly increases to a value of 120 mg/dm^3, irrespectively of the concentration of phosphogypsum in the medium, and then it smoothly drops to a level below 10 mg/dm^3 – also in the reference sample. The presence of phosphogypsum only extends the time needed for its decomposition (Kornaros et al. 1996)..

The process of denitrification is of great importance in agriculture (soil deficiency in biologically useful nitrogen), in this context the results of the study indicate that the use of phosphogypsum for field cultivation should not disturb the cycle of nitrogen conversions in the soil. Similarly, the presence of phosphogypsum in water reservoirs will not cause an over-accumulation of difficult to remove nitrates (V) and nitrates (III).

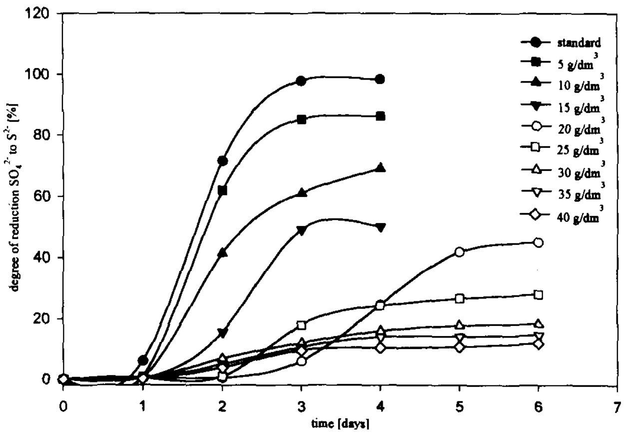


Fig. 2. The influence of the concentration of phosphogypsum on the dissimilatory sulphates reduction proces carried out with *Desulfotomaculum ruminis* bacteria (pH = 7.0, 37^{o}C, C/S = 3.2)

Fig. 2 presents results of a study on the effect of the concentration of phosphogypsum on desulfurication taking place in the medium in the presence of *Desulfotomaculum ruminis* bacteria. This species is the best known mezophilous bacteria living at a neutral pH and capable of using many different organic compounds in the process of reduction of sulphates and for this reason often used in studies on utilisation of wastes and purification of sewage (Szulczynski et al. 1987, Waligórska et al. 2000, Walenciak et al. 1999).

The kinetic curves of biotransformation of phosphogypsum used at concentrations up to 15 g/dm^3 in a lactate medium have a similar shape corresponding to typical phases of micro-organisms multiplication, that is to the induction period, phase of logarithmic growth, equilibrium phase and stabilisation of the process. In this range of concentrations the induction period is more or less the same and takes about 24h. With increasing concentration of phosphogypsum, from 5 to 15 g/dm^3, the degree sulphate reduction systematically decreases reaching 45% in the medium containing 15 g phosphogypsum per dm^3. A further increase of its concentration causes a pronounced inhibition of the process of sulphate reduction reaching a level of 10% in a medium containing 40 g phosphogypsum per dm^3, Fig. 2.

Thus, it has been shown that the phosphogypsum tested (from Police Chemical Plant) can be used as a substrate for sulphates reducing bacteria. In a medium containing up to 15 g/dm^3 of the phosphogypsum, in the presence of lactate at a C/S ratio of 3.2, it can be suggested that the phosphogypsum is decomposed into, among others, calcium carbonate and hydrogen sulphide. This process might be described as follows:

$$\underset{\text{(phosphogypsum)}}{CaSO_4 \cdot 2H_2O} + \underset{\text{(organic compound)}}{2(CH_2O)} \xrightarrow{BRS} Ca^{2+} + CO_2 + H_2O + \uparrow H_2S$$

The hydrogen sulphide released precipitates the metal ions contaminating the phosphogypsum and neutralised the pathogens which could occur in the medium. Moreover, the produced metal sulphides and hydrogen sulphide can be subjected to biological oxidation with the use of the genus *Thiobacillus* bacteria, according to the scheme [8]:

$$2MeS_2 + 2H_2O + 7O_2 \xrightarrow[Thiobacillus]{} 2MeSO_4 + 2H_2SO_4.$$

Therefore, as has been shown, biotransformation of the waste phosphogypsum can be a double blessing: it enables a decomposition of a harmful waste and oxidation of organic contaminants introduced into the reaction medium. The evidence presented allows us to claim that there is a real possibility of realisation of the above process of utilisation of the phosphogypsum and oxidation of the organic substrate present in e.g. agricultural waste.

Table 2**.** TOC reduction and degree of dissimilatory sulphates reduction in the medium containing different amounts of Morocco phosphogypsum with *Desulfotomaculum ruminis* bacteria (T = 37^{o}C, C/S = 3.2)

Concentration of Morocco phosphogypsum in the medium [g/dm^3]	Proces duration [days]	Degree of SO_4^{2-} reduction [%]	TOC decrease [%]
0.0	3	100	-
5.0	3	91	47.5
10.0	4	76	56.2
15.0	4	55	64.8
20.0	6	49	72.7
25.0	6	35	76.2
30.0	6	26	76.2
35.0	7	22	76.2
40.0	7	19	76.2

Table 2 gives the results of the study on the decrease of TOC at a certain degree of conversion of sulphates from the phosphogypsum. As follows from the data, at the phosphogypsum concentrations up to 5g/dm^3, the degree of conversion is close to

90%, and the corresponding TOC decrease is close to 50%. For a series of experiments conducted at higher concentrations of the phosphogypsum - up to 40 g/dm^3, TOC decrease reaches over 76%.

CONCLUSIONS

The above presented results of the preliminary study have shown that the phosphogypsum tested (Police Chemical Plant) is not toxic towards the bacteria *Bacillus licheniformis* and can be used as a substrate for *Desulfotomaculum ruminis*. The phosphogypsum can act as electron acceptor in the processes of oxidation of simple organic substances and thus can be used for purification of reservoirs with water characterised by excess amounts of organic carbon. In all series of the experiments, desulfurication in media containing up to 10 g/dm^3 of the phosphogypsum at the C/S ratio if 3.2, the degree of conversion was 80-90%, and TOC decreased by 47-57%. The laboratory tests conducted in the optimum conditions have proved that after 10 days the reduction of the phosphogypsum gives about 2g of sulphide sulphur in 1 dm^3 of the medium containing lactate (Juszczak et al.) . All the results indicate a real possibility of biotransformation of this waste on a large scale. The project would require low investment cost and would bring additional profit of sewage waste purification - a decrease of TOC, especially the waste of agricultural origin. The phosphogypsum tested should not be used directly in agriculture because of strongly acidic pH and the content of metal ions, which could be harmful for cultivation.

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K. Seifert, A. Moska, F. Domka, *Wpływ odpadowego fosfogipsu na proces denitryfikacji i redukcji siarczanów*, Fizykochemiczne Problemy Mineralurgii, 36, (2002), 209-216 (w jęz. ang.)

Badano wpływ odpadowego fosfogipsu, powstającego podczas produkcji kwasu fosforowego z apatytów i fosforytów, na procesy denitryfikacji oraz dysymilacyjnej redukcji siarczanów, zachodzące z wykorzystaniem bakterii z rodzaju *Bacillus* oraz *Desulfotomaculum.*

Wykazano, że w określonym zakresie stężeń testowany fosfogips nie działa toksycznie na proces namnażania bakterii i stanowi źródło siarczanów dla bakterii *Desulfotomaculum.* Ponadto stwierdzono, że może on pełnić rolę akceptora elektronów w procesach utleniania prostych substratów organicznych w procesie bioredukcji azotanów lub siarczanów. W optymalnych warunkach dysymilacyjnej redukcji siarczanów, zachodzącej w podłożu zawierającym fosfogips, substrat organiczny oraz bakterie *Desulfotomaculum ruminis*, stopień przemiany kształtuje się na poziomie 90%, a ubytek ChZT wynosi około 50%.