RESEARCH PAPERS
FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA
SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

2015 Volume 23, Number 36

3,5-DICHLOROPHENOL REMOVAL FROM WASTEWATER USING ALTERNATIVE ADSORBENTS

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Abstract

The main objective of this paper is to evaluate the efficiency of 3,5-dichlorophenol removal from wastewater by using alternative low cost adsorbents. Waste from the production and processing of metals (black nickel mud, red mud) and a biosorbent (Lemna minor) were used for this research. Initial concentration of the contaminant was 4 mmol L^{-1}, the contact time of sorbent and waste water was 0 - 48 hrs and the temperature during experiment was 25 ± 0.2 °C. The results show that the highest removal efficiency of 3,5 - dichlorophenol (58.18 %) was reached by the red mud in 48 hours.

Key words

red mud, black nickel mud, Lemna minor, sorption, adsorbent

INTRODUCTION

Chlorophenols are organic compounds consisting of a benzene ring, OH- group and chlorine atoms. The whole group of chlorophenols includes dozens of compounds different in molecular structure, chemical and physical properties and particularly in toxicity. Researches of the environmental pollution status conducted around the world have confirmed the presence of chlorophenols in many ecosystems: in surface and underground waters, in bottom sediments, in atmospheric air and in soil. Pollution of these ecosystems is caused by various applications of chlorophenols in the industry, particularly during the manufacture of herbicides(e.g. Triadimefon), pesticides, insecticides, fungicides, wood preserves, disinfectants (e.g. Triclosan), pharmaceuticals and coloring agents. Chlorophenols are also formed during water disinfection by chlorine (1).

Degradation and removal of chlorophenol is accomplished by various methods. Several technologies that have been proposed for the degradation and removal of chlorophenol, can be divided into the following groups: physical methods, chemical methods, electrochemical processing and ɤ - irradiation, photochemical degradation and microbial degradation (2).

MATERIALS AND METHODS

Experiment description

Figure 1 shows the main scheme of the experiment used for the efficient concentration reduction of 3,5-dichlorophenol removal form wastewater by using alternative low-cost adsorbents. Selected adsorbents used for this removal are: red mud, black nickel mud and *Lemna minor* with batch size of 0.1 g:

- Red mud (Sereď - waste of metal production),
- Black nickel mud (Žiar n. Hronom. - waste of metal production),
- Lemna minor (biosorbent).

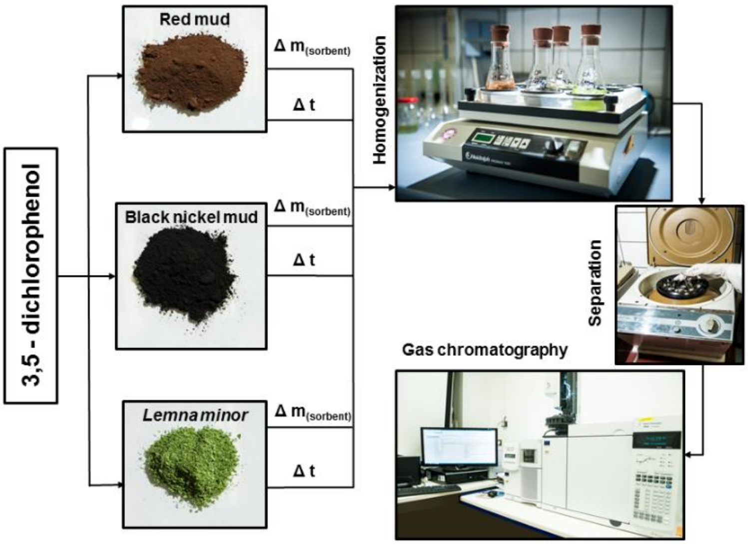

Fig. 1 *Working procedure scheme of 3,5-dichlorophenol reduction*

For the determination of 3,5-dichlorophenol concentration loss a gas chromatograph with MS detector GC-MS Agilent 5975C equipped with capillary column (30 m x 0.250 mm - inner diameter) with film of 0.25 μm and helium mobile phase was used. Parameters were chosen for the method of phenolitic compounds determination by the EPA Methods 82 70. Figures 2, 3 and 4 show the graphical representation of 3,5-dichlorophenol sorption by black nickel mud, red mud and biosorbent *Lemna minor*. The efficiency percentage of the process at different times and types of sorbent is shown in the Tables 3, 4, 5. The starting concentration of the 3,5-dichlorophenol was 4 mmol L^{-1}.

Characteristics of sorbents

Red mud. During the production of aluminium oxide, solid waste is formed: brown sludge from the production process of Al_2O_3 by sintering method, and red mud from the production of Al_2O_3 by Bayer process, wherein the bauxite at elevated pressure and temperature, is leached with sodium hydroxide. After clarification, dissolved sodium aluminate is precipitated and calcined in the next steps (3). Both types of the sludge are stable mixtures of chemical compounds with a stable structure and known chemical composition (4, 5).

The red mud composition is shown in Table 1. Chemical composition and quantity of the red mud varies depending on what location and production process it originates from.

CHEMICAL COMPOSITION OF RED MUD (6) Table 1

Chemical composition [%]	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	K_2O	Sc_2O_3	V_2O_3	Nb_2O_5	Loss
Bayer process	26.41	18.94	8.52	21.84	4.75	7.40	0.068	0.76	0.34	0.008	9.71
Sintering process	7.95	10.36	1.29	40.22	3.53	7.14	0.053	0.16	0.024	0.020	12.95

Black nickel mud. Black nickel mud is a waste from the production process of the nickel and cobalt-based Albanian imported iron-nickel lateritic ores containing 1 % of nickel in one tone. It is a soft material with a predominant fraction below 0.01 mm. Nickel smelter in Sereď had processed the Albanian iron-nickel ore during its existence since the year 1963 (7, 8).

Black nickel mud containing chromium and nickel residues is essentially an iron concentrate with chemical composition shown in Table 2 (9).

CHEMICLA COMPOSITION OF BLACK NICKEL MUD (9) Table 2

Chemical composition [%]	Fe	Cr_2O_3	SiO_2	Al_2O_3	CaO	P_2O_3	Ni
Caron process	50 - 80	3.2 - 3.5	6 - 8	6 - 8	2.5 - 3.5	0.06 - 0.18	0.28 - 0.30

Lemna minor. Lemna minor is one of the smallest flowering plants in the world, often not bigger than 10 mm. It is abundantly present in almost the entire territory of our country from planar to montane stages. Duckweed has a potential in the purification of wastewater, absorbing excess nutrients from surface water, including phosphorus and ammonia (10, 11, 12 and 13). It has a fan-shaped body consisting of 1 - 3 leaves. One radicle protrudes from each individual fan-shaped body plant. It tends to grow in dense colonies in calm water where more types of duckweeds often coexist (14).

In recent years, the use of biological material from living or dried degradation of heavy metals comes to the fore, mainly because of its low cost, natural and abundant occurrence and high efficiency in metals biosorption. Their main advantage is that the dried cells accumulate heavy metal ions in the same or even higher levels than the living cells and they can be stored at room temperature (15). Duckweed has excellent accumulation capabilities, mainly observed in the compounds of nitrogen, phosphorus and heavy metals (16). Low price biomaterials with a short-period and asexual reproduction and suitable assumptions on pesticides biosorption can be successfully used in the degradation of pesticides in water ecosystems.

RESULTS AND DISCUSSION

Figure 2 displays the resulting graphs where, depending on the time of the detector signal, we can observe the decrease of the detector signal according to the exposure time of the sorbent black nickel mud. The lowest response of the detector when measuring 3,5-dichlorophenol was observed at the exposure time of 48 hours using black nickel mud.

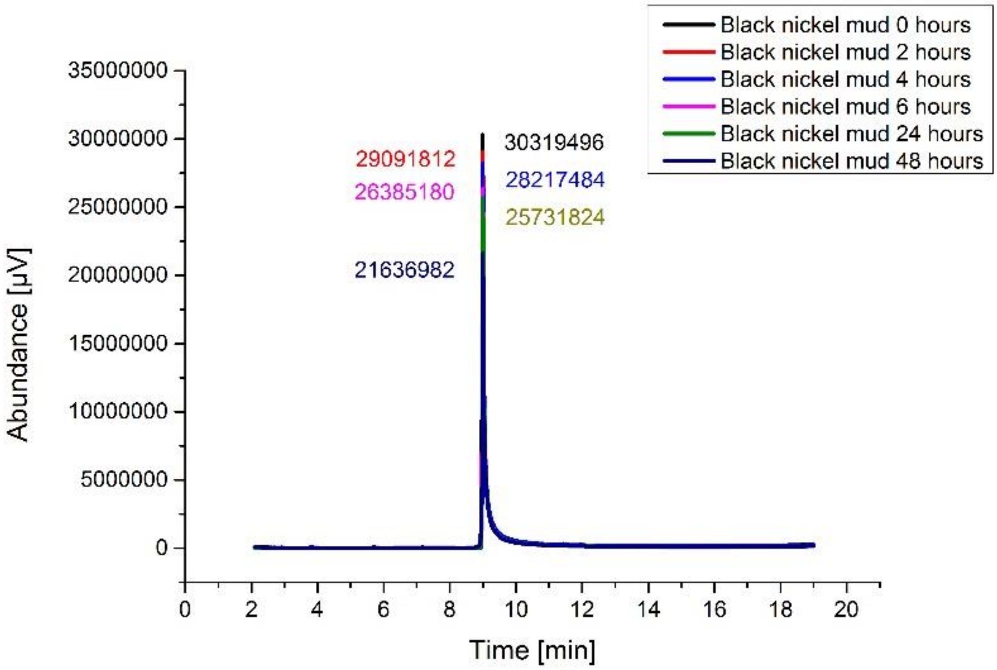

Fig. 2 *Sorption of 3,5-dichlorophenol using black nickel mud*

In Table 3, we can see that the efficiency of black nickel mud at the exposure time of 2 hours was only about 4 %, but the efficiency raised with a longer exposure. After 48 hours, the effectiveness of the sorbent was around 28.64 %.

EFICIENCY OF 3,5-DICHLOROPHENOL DEGRADTION
BY BLACK NICKEL MUD

Table 3

	Abundance [µV]	**Efficiency [%]**
Sample t = 0 h	30 319 496	0.00
Sample t = 2 h	29 091 812	4.04
Sample t = 4 h	28 217 484	6.93
Sample t = 6 h	26 385 180	1.98
Sample t = 24 h	25 731 824	15.13
Sample t = 48 h	21 636 982	28.64

In Figure 3, we can see dependence of the detector signal from time-chromatogram. Decrease of the chlorophenol concentration versus the exposure time of the red mud sorbent can be observed. Similarly to the previous measurements, the lowest concentration of chlorophenol (Figure 2) was measured at the exposure time of 48 hrs.

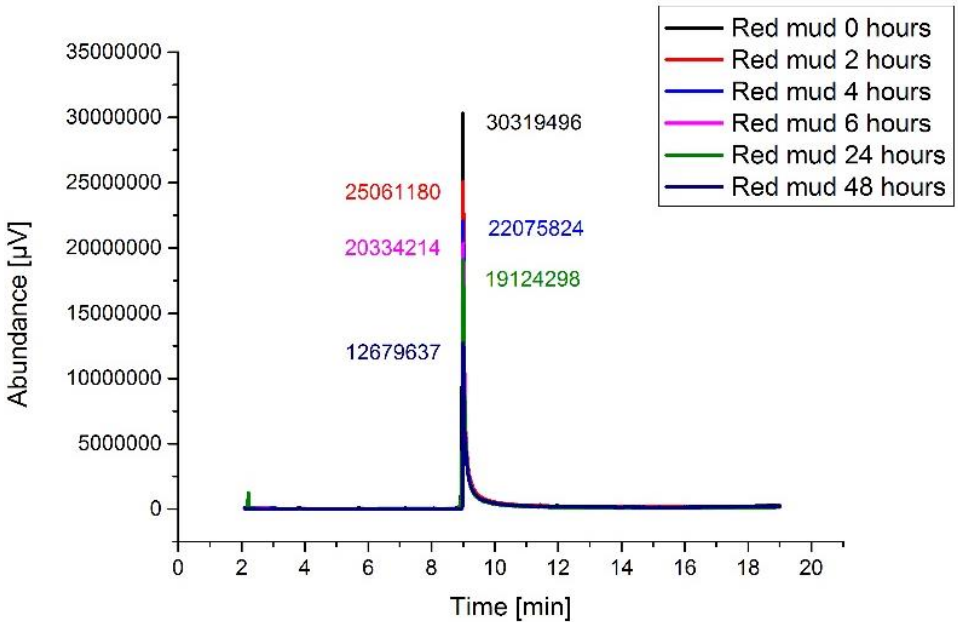

Fig. 3 *Sorption of 3,5 - dichlorophenol using red mud*

In Figure 3, we can see that the efficiency of the red mud sorbent reached approximately 17.34 % after 2 hours, but during a longer period of time compared to the previous measurement. The efficiency of reducing the contaminants using red mud was gradually increasing until at the exposure time of 48 hours when the efficiency reached 58.18 %.

EFICIENCY OF 3,5-DICHLOROPHENOL DEGRADTION BY RED MUD Table 4

	Abundance [µV]	**Efficiency [%]**
Sample t = 0 h	30 319 496	0.00
Sample t = 2 h	25 061 180	17.34
Sample t = 4 h	22 075 824	27.19
Sample t = 6 h	20 334 214	32.93
Sample t = 24 h	19 124 298	36.92
Sample t = 48 h	12 679 637	58.18

Figure 4 shows fading of the detector signal versus the exposure time of the biosorbent *Lemna minor*. During prolonged exposure of the *Lemna minor* sorbent, response of the detector was reduced.

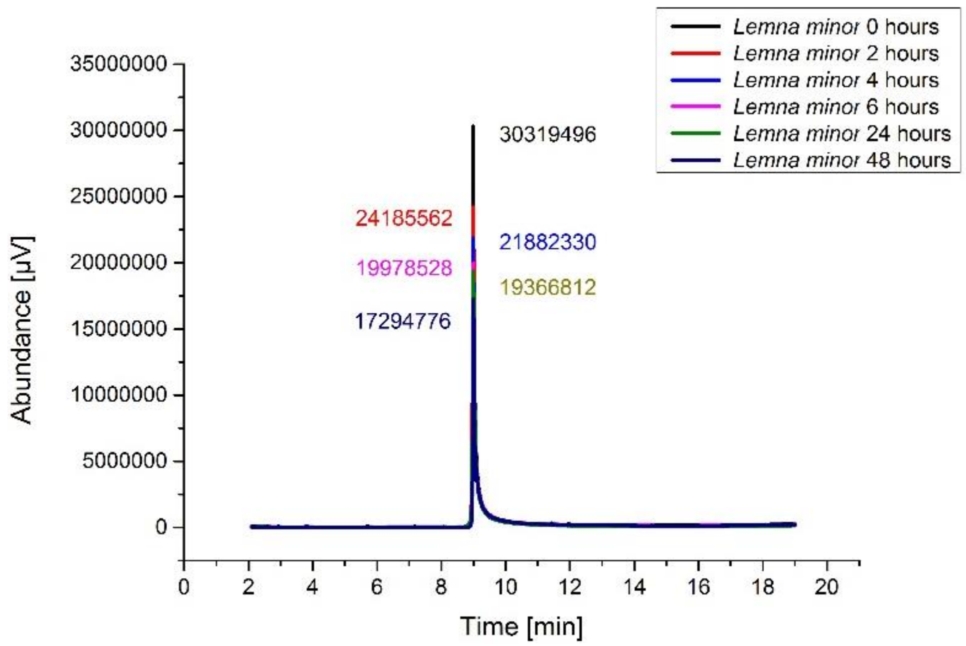

Fig. 4 *Sorption of 3,5-dichlorophenol using Lemna minor*

In Table 5, we can see that, after 2 hours, the efficiency of the *Lemna minor* sorbent reached approximately 20.23 %. During longer period of exposure, the efficiency of contaminant reduction was gradually increasing. After 48 hours, the efficiency of the sorbent was 42.96 %.

EFICIENCY OF 3,5-DICHLOROPHENOL DEGRADTION BY *LEMNA MINOR* Table 5

	Abundance [μV]	**Efficiency [%]**
Sample t = 0 h	30 319 496	0.00
Sample t = 2 hrs	24 185 562	20.23
Sample t = 4 hrs	21 882 330	27.83
Sample t = 6 hrs	19 978 528	34.11
Sample t = 24 hrs	19 366 812	36.12
Sample t = 48 hrs	17 294 776	42.96

CONCLUSION

One of the basic criteria of the remediation procedures' applicability in practice are its financial requirements. Therefore, nowadays, we can observe a growing trend of using alternative low-cost sorbents in response to replace traditional remediation methods and the sorbents which are effective in removing pollutants, but relatively expensive.

Low-cost sorbents comprise the following sorbents: red mud, black nickel mud and *Lemmna minor* biosorbent, which provide a response to the problem of alternative sorbents usage.

Sorbents were examined at the room temperature of 25 °C, based on the scheme prepared according to working procedure. All of the studied sorbents effectively reduced the concentration of 3,5-dichlorophenol, whereby we observed that the best results were obtained during longer exposure times. The highest efficiency was achieved by the red mud (58.18 % after 48 hrs), followed by *Lemna minor* (42.96 % after 48 hrs) and black nickel mud (28.64 % after 48 hrs).

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