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THE USE OF RED MUD AND BLACK NICKEL MUD IN SORPTION OF 3,5-DICHLOROPHENOL

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Abstract

This article discusses the use of alternative inexpensive adsorbents – wastes from the metal production - red mud (RM) and black nickel mud (BNM) and their sorption efficiency in 3,5-dichlorophenol removal. Chlorophenols are organic compounds consisting of a benzene ring, OH groups and chlorine atoms. The effects of adsorbent dose, contact time, and temperature on sorption process were monitored. The results showed that the optimal conditions to achieve the highest sorption efficiency of 3,5-dichlorophenol were reached with the use of black nickel mud at the amount (2.0 g), sorption time (1 hour) and at increased temperature (45 °C). The sorption efficiency under these conditions was 87.99 %. With increasing sorption time, the sorption efficiency decreased and desorption occurred. The same behaviour was observed using red mud of the same amount (2.0 g) at the same temperature (45 °C); however, after 1 hour, sorption efficiency was slightly reduced (85.16 %) compared to black nickel mud. Anyway, both of used materials are suitable for the use as alternative sorbents of 3,5-dichlorophenol under suitable conditions.

Keywords

Red mud, black nickel mud, 3,5-dichlorophenol, sorption efficiency

INTRODUCTION

Chlorophenols are environmental pollutants introduced into the environment especially from the chemical and pharmaceutical industry activities [1]. It is a diverse group of chlorinated phenols. They are commonly used as pesticides, disinfectants, and as chemical intermediates in the production of more complex chemical. The main sources of chlorophenols from these human activities are pesticides [2]. 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 [3]. They are classified into five types based on the number of Cl-atoms attached to the benzene ring at specific positions to the hydroxyl group. There are 19 possible chlorophenol compounds including monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols and pentachlorophenols containing 1, 2, 3, 4 and 5 Cl-atoms attached to the benzene ring. All these chlorophenols are soluble in alcohols, ethers, carbon tetrachloride, benzene, acetone, acetic acid, and sodium hydroxide, but all are sparingly soluble in water [4]. Chlorophenols show mutagenic and carcinogenic effect and are poorly biodegradable even at trace levels [5] by high vapour pressure even at the room temperature. They are widely used as preservatives in the pesticide, herbicide, and paper industries. These applications often lead to the wastewater and ground water contamination, which can pose risk to public health when contamination of drinking water supplies occurs. Therefore, they are included in both, the U.S. Environmental Protection Agency and the European Union list of priority pollutants [6]. The existence of chlorophenols in drinking water causes unpleasant taste and odour even at the concentration as low as 0.1 mg/L [7]. Accordingly, the US Environmental Protection Agency and the WHO recommended that the amount of chlorophenols must not exceed 0.5 μg/L in drinking water and 100 μg/L in industrial wastewater [8].

One of the processes for the removal of chlorophenols is sorption owing to its inexpensiveness, high efficiency, ease of operation and applicability. It may also remove soluble and insoluble organic pollutants, and the removal capacity by sorption may be up to 99.9 %. Therefore, sorption has been used for the removal of a variety of organic pollutants from various contaminated water sources [5, 9]. Development of inexpensive adsorbents from industrial wastes for the treatment of wastewaters is an important area in environmental sciences. Blast furnace slag, dust or mud from the waste metal production, have been utilized as inexpensive adsorbents for the removal of phenols which represent an important class of pollutants as they are highly toxic [11]. Red mud and black nickel mud can be converted into inexpensive potential adsorbent, and this final material can be used for the removal of chlorophenol from wastewater [12].

MATERIALS AND METHODS

This article discusses the use of alternative inexpensive adsorbents from the metal production - red mud (RM) and black nickel mud (BNM), and their sorption efficiency of 3,5-dichlorophenol.

Red mud (RM) is an industrial waste (by-product) produced in large amounts during the production of aluminium oxide from the bauxite at elevated pressure and temperature, leached with sodium hydroxide (the Bayer process). Its disposal generates serious environmental pollution which is due to high alkalinity [3, 10]. This highly alkaline waste material has a pH of 10-13 because of the sodium hydroxide solution used in the refining process [13].

However, chemical composition and also quantity of the RM vary depending on the location and production process they originated from [3, 10]. RM is mainly composed of fine particles containing aluminium, iron, silicon, titanium oxides and hydroxides. The red colour is

caused by the oxidized iron present, which can make up to 60 % of the mass of the RM [13]. RM usually contains many residual minerals from bauxite. Soldán and Kobetičová (2015) investigated the chemical composition (Table 1) of adsorbents by using a EDX analysis. In RM they identified anatas (TiO_2), hematite (Fe_2O_3), limestone ($CaCO_3$), halloysite ($Al_2Si_2O_5(OH)_4$) and gibbsite ($Al(OH)_3$). Wang et al. (2019) according to Ascensão´s et al. (2017) article, lists the chemical compositions of RM when using different production methods (Bayer, sintering, and combined process). Table 2 shows the differences.

Table 1 Chemical elements of RM and BNM [14]

Adsorbent	O [%]	Al [%]	Si [%]	Mg [%]	Ca [%]	Ti [%]	Fe [%]
Red mud	34.31	7.74	5.02	-	11.48	2.6	38.83
Black nickel mud	25.31	4.97	4.56	3.48	3.70	-	67.29

Table 2 Differences between chemical compositions of RM using different production methods (%) [10, 15]

Chemical Constituent	Fe_2O_3	Al_2O_3	SiO_2	CaO	Na_2O	TiO_2	K_2O	MgO	Sc_2O_3	Nb_2O_5	Loss
Bayer process	13.69	7.02	18.1	42.21	2.38	2.1	0.3	-	-	-	-
Combined process	10.97	7.68	22.67	40.78	2.93	3.26	0.38	1.77	-	-	11.77
Sintering process	11.4	10.66	21.06	40.62	1.49	-	0.45	0.93	-	-	6.86

RM is a very fine material in terms of particle size distribution, having an average particle size <10 μm. It has porous surface and contains various particles of different size and shape. Typical values would account for 90 % volume below 75 μm. The specific surface area (BET) of RM is around 10-25 $m^2\ g^{-1}$. Figure 1 shows morphology (SEM photos) of RM [16]. For instance, RM may be transformed into useful product, such as sorbent. However, emphasis is placed on the surface modification to obtain high sorption [3, 10]. In Slovakia, aluminium oxide was produced mainly by sintering in the aluminium mill in Žiar n. Hronom [17]. RM used in the present experiments was supplied from Žiar n. Hronom.

The complex of the former Nickel Smelter in Sereď Town located in the Podunajská rovina on the border between two cadastral territories of Sereď and Dolná Streda. The black nickel mud (BNM) was produced using the technology of wet Caronprocess in processing the Albanian iron-nickel ore. The production in Nickel Smelter (1963–1993) took 30 years, and it stopped for the economic and ecological reasons. Area of the landfill BNM has 35 ha, and the volume of BNM is almost 9 mil. tons. The chemical composition of BNM is: Fe (50-80 %), Cr_2O_3 (2.5-3.5 %), SiO_2 (6-8 %), Al_2O_3(6-8 %), CaO (2.5- 3.5 %), Ni (0.17 %), P_2O (0.6-0.18 %) [18]. The BNM mud is of fine texture and unnatural black coloration, and contains 17.5 % particles smaller than 10 μm airborne dust, which is respirable dust [19], and also contains heavy metals (e.g. Cr-approx. 3 %). Figure 2 shows morphology (SEM photos) of BNM [22]. Therefore, the highest danger is polymetallic dust which spreads into the environment [20]. The BNM is a very porous material with total porosity of 68 vol % [21]. Due to its large specific surface area, it is uses as a sorbent and coagulant in the remediation of waters in agriculture and also in the technology of wastewater cleaning and in chemical industry [20]. BNM used in the present experiments was supplied from Sereď.

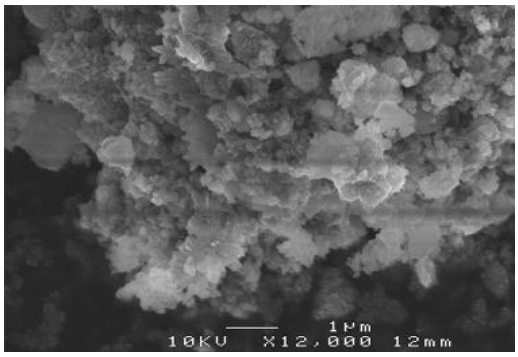


Figure 1 *SEM photo of RM [16]*

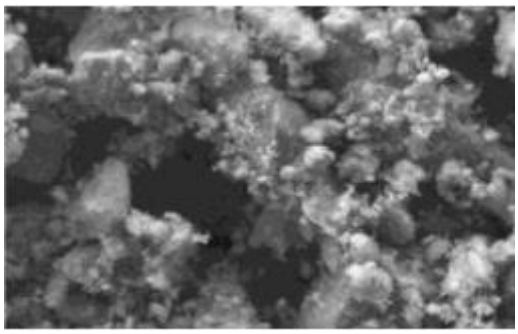


Figure 2 *SEM photo of BNM (fraction < 500 µm).*
Detail of the surface at magnification of 1000 time [22].

At first, physico-chemical pretreatment of both sorbents was performed Acidification methods improve the sorption capacity of RM and BNM by dissolving the calcium and acid-soluble salts, which create new cavities and increase the surface area. The acid used for this purpose was concentrated hydrochloric acid. To 10.0 g of sorbent 190 ml of distilled water and 10 ml of concentrated hydrochloric acid were added. The suspension was boiled at 100 °C for 20 minutes. After that, 25 ml of ammonium hydroxide was added. The suspension was cooled to the room temperature and filtered. The chemical pretreatment was followed by drying the filter residue in an oven at 100 °C. The residue was ground in a mortar.

3,5-dichlorophenol solution was prepared at a concentration of 20 mg/L. 100 ml of the 3,5-dichlorophenol solution was placed into the Erlenmeyer flasks, and 1.0 and 2.0 g of ground filter residue of RM and BNM was added. In the experimental part, the efficiency of the sorption with the sorbents and the influence of the sorption conditions were observed.

To achieve the required temperature, the samples were placed in a Binder laboratory sterilizer for a specified time of 1, 2, 3, 24, 48, 72 and 96 hours. Subsequently, the samples were placed to the Nahita centrifuges (model 2640/12) for 5 minutes. Rotational speed was 4000 rpm to sediment the small, undesirable particles of sorbent. The sorption efficiency of 3,5-dichlorophenol was determined by measuring the absorbance of the solutions after sorption in 1 cm plastic cuvettes using GENESYS 8 in UV / VIS area spectrophotometer (190 nm – 400 nm).

RESULTS AND DISCUSSION

As can be seen in Figure 3 for 1.0 g of RM, the highest sorption efficiency was achieved by RM at the temperature of 45 °C (81.62 % after 3 h). Adsorption at 35 °C is not very effective. We can see that the temperature and the contact time of sorbate and sorbent have a relatively high impact on the efficiency of sorption process. However, desorption occurred after 72 hours

at 20 °C (from 77.74 % to 57.24 %) and 45 °C (from 80.21 % to 49.82 %). However, desorption was not observed at 35 °C. This phenomenon can be probably caused by the surface interactions between the sorbent and the captured substance (the lowest at 35 °C), while increasing again with a further increase of temperature. The saturation of the surface with the captured substance is fast at the temperatures of 25 and 45 °C, and reaches the maximum within about 2 hours.

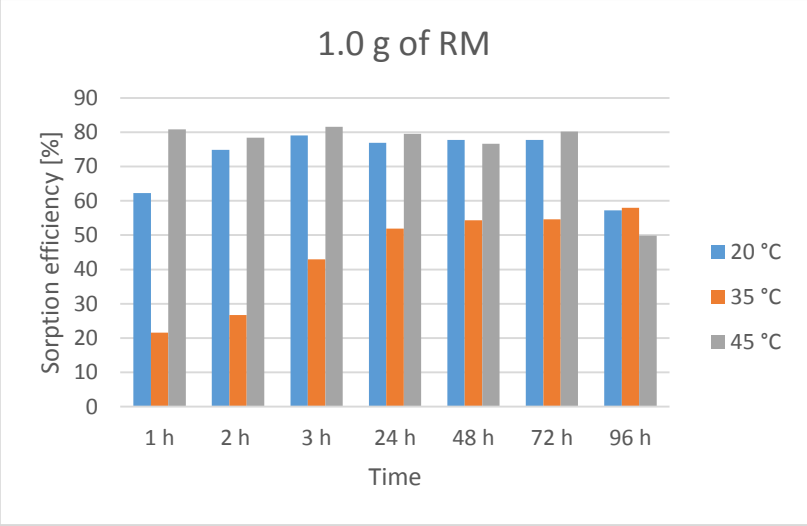


Figure 3 *Comparison of the sorption efficiency of 3,5-dichlorophenol with 1.0 g of RM at temperatures of 20, 35 and 45 °C*

On the other hand, gradual desorption can be observed in Figure 4 after 3 hours of sorption at 45 °C and 2.0 g of RM added. Similarly to 1.0 g of RM, also with 2.0 g of RM at 35 ℃ no desorption was not observed, while sorption efficiency increased very slowly. 2.0 g of RM at 20 ℃ has caused decrease of sorption efficiency of 3,5-dichlorophenol from 24 to 48 hours (72.79 % to 68.9 %) with desorption occurring after 72 hours.

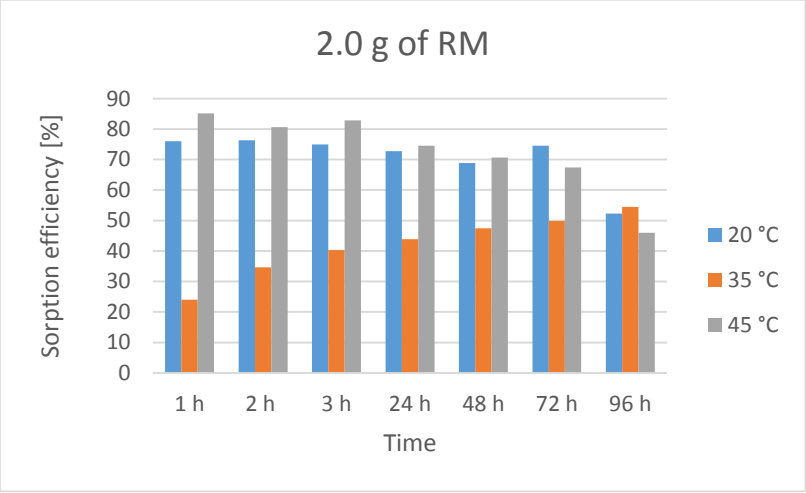
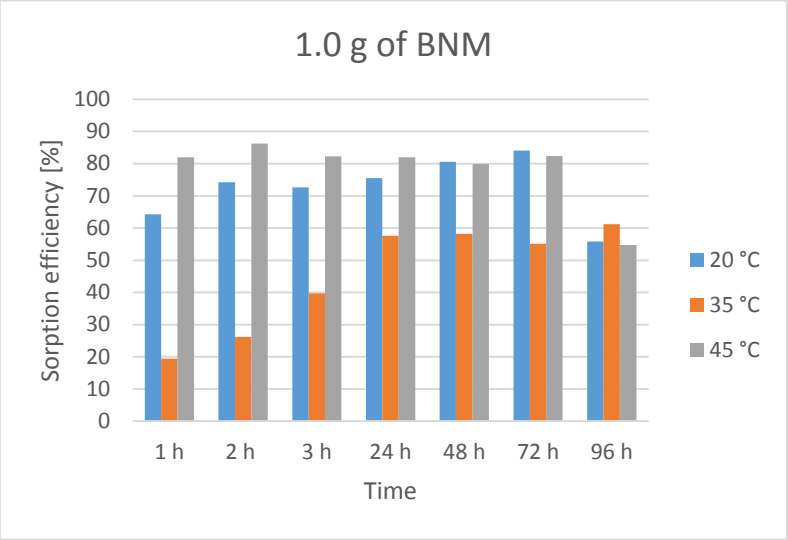


Figure 4 *Comparison of the sorption efficiency of 3,5-dichlorophenol with 2.0 g of RM at temperatures of 20, 35 and 45 °C*

The sorption efficiency of 1.0 g of BNM added increased very slowly at the same temperature, but after 96 h, desorption has occurred, as can be seen in Figure 5. The results for 1.0 g of BNM at 35 ℃ are not that interesting as in the previous Figures 3 and 4. In spite of the fact that the relatively high sorption efficiency was measured using 1.0 g of BNM at 45 °C, 2.0 g of BNM showed better result for sorption of 3,5-dichlorophenol solution at the same

temperature. The sorption efficiency of 2.0 g of BNM is shown in Figure 6. The highest efficiency was achieved by 2.0 g of BNM added (87.99 % after 1 h). However, desorption occurred slowly after 1 hour of sorption.



Figue 5 *Comparison of the sorption efficiency of 3,5-dichlorophenol with 1.0 g of BNM at temperatures of 20, 35 and 45 °C*

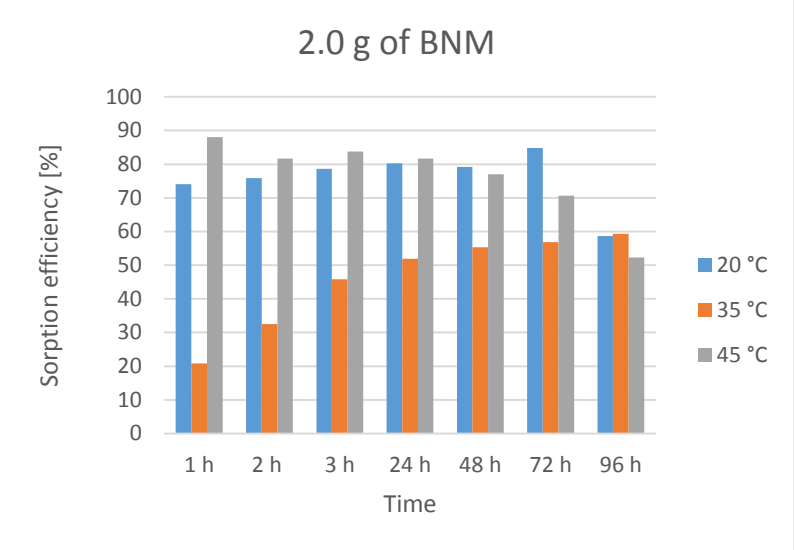


Figure 6 *Comparison of the sorption efficiency of 3,5-dichlorophenol with 2.0 g of BNM at temperatures of 20, 35 and 45 °C*

As claimed by Wang at al. (2019) in his review about application of RM in wastewater treatment, the RM adsorbs phenolic compounds because it has a positive surface charge that attracts negatively charged phenols.

In this paper, both of adsorbents (RM and BNM) were physico-chemical treated. For example, Kobetičová et al. (2017) reached the highest efficiency of 3,5-dichlorophenol sorption 95.62 % using RM (2.5 g) with sorption time 48 hours at 25 °C. In their experimental measurement, the effect of temperature on the efficiency of sorption did not demonstrate a significant effect. Their pretreatment of RM samples was used to remove possible organic impurities, which could negatively affect the sorption properties. The sorbent was annealed in

a muffle furnace at the temperature of 500 °C during 2 hours. Therefore, the requirements for treatment of sorbent may vary.

CONCLUSION

Red mud and black nickel mud (inexpensive sorbents) were investigated for removal of 3,5-dichlorophenol from water solution. The physico-chemical treatment of selected sorbents was performed before the sorption process. Experimental data showed the efficiency of the sorption influenced by the amount of the sorbent (the observed amounts were 1.0 g and 2.0 g) and by the contact time of the sorbent and the sorbate (the observed times 1, 2, 3, 24, 48, 72 and 96 hours) and also by temperature (the observed temperatures 20, 35 and 45 °C). It was found, that the optimal conditions to achieve the highest sorption efficiency of 3,5-dichlorophenol were using black nickel mud at the amount (2.0 g), sorption time (1 hour) and temperature (45 °C). The sorption efficiency under these conditions was 87.99 %. With increasing sorption time, the efficiency decreased and desorption occurred. The same behaviour was observed using red mud of the same weight (2.0 g) and at the same temperature (45 °C); however, after 1 hour, the sorption efficiency was more reduced (85.16 %) than in the case of using black nickel mud. With increasing both, temperature and a sorbent amount, the sorbent efficiency increased. The lowest achieved sorption efficiency by both adsorbents was observed at 35 °C, the sorption was significantly reduced compared to 20 °C and 45 °C. We recommend using black nickel mud for practical use especially at 45 °C. Anyway, both of the used sorbents are effective in 3,5-dichlorophenol removal under defined conditions.

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