Journal of Hazardous Materials 271 (2014) 65–72

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Modified clay minerals efficiency against chemical and biological warfare agents for civil human protection

Daniela Plachá [a,c,*], Kateřina Rosenbergová [b], Jiří Slabotínský [b], Kateřina Mamulová Kutláková [a], Soňa Študentová [d], Gražyna Simha Martynková [a]

[a] Nanotechnology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15, Poruba, Ostrava 708 33, Czech Republic
[b] National Institute for NBC Protection, Kamenná 71, Milín 262 31, Czech Republic
[c] Energy Units for Utilization of non Traditional Energy Sources, VŠB-Technical University of Ostrava, 17. listopadu 15, Poruba, Ostrava 708 33, Czech Republic
[d] Regional Materials Science and Technology Centre, VŠB-Technical University of Ostrava, 17. listopadu 15, Poruba, Ostrava 708 33, Czech Republic

HIGHLIGHTS

- The efficient composite materials against chemical warfare agents such as yperite.
- The efficient materials against biological warfare agents such as *Yersinia pestis*.
- Efficient alternative material for protective clothing or filtration equipment.
- Material efficiency can be tailored according to the needs.

ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form 23 January 2014
Accepted 25 January 2014
Available online 12 February 2014

Keywords:
Yperite
Mustard gas
Antibacterial activity
Permeation
Clay mineral

ABSTRACT

Sorption efficiencies of modified montmorillonite and vermiculite of their mono ionic Na and organic HDTMA and HDP forms were studied against chemical and biological warfare agents such as yperite and selected bacterial strains. Yperite interactions with modified clay minerals were observed through its capture in low-density polyethylene foil-modified clay composites by measuring yperite gas permeation with using chemical indication and gas chromatography methods. The antibacterial activities of synthetized organoclays were tested against selected Gram-positive and Gram-negative bacterial species in minimum inhibitory concentration tests. The obtained results showed a positive influence of modified clay minerals on the significant yperite breakthrough-time increase. The most effective material was the polyethylene-Na form montmorillonite, while the polyethylene-Na form vermiculite showed the lowest efficiency. With increasing organic cations loading in the interlayer space the montmorillonite efficiency decreased, and in the case of vermiculite an opposite effect was observed. Generally the modified montmorillonites were more effective than modified vermiculites. The HDP cations seem to be more effective compare to the HDTMA. The antibacterial activity tests confirmed efficiency of all organically modified clay minerals against Gram-positive bacteria. The confirmation of antibacterial activity against *Y. pestis*, plague bacteria, is the most interesting result of this part of the study.

1. Introduction

Chemical (CWA) and biological (BWA) warfare agents are perpetually a low-probability but high-impact risk to the military and the civilian population [1,2]. This fact was confirmed in the 1990s, when the proliferation of these agents to the terrorist groups was a warning. The globalisation and escalations of terrorist attacks in recent times induced the necessity to include these threats to national and international emergency and risk management plans

* Corresponding author. Tel.: +420 597 321 575; fax: +420 597 321 640.
E-mail addresses: daniela.placha@vsb.cz (D. Plachá), rosenbergova@sujchbo.cz (K. Rosenbergová), slabotinsky@sujchbo.cz (J. Slabotínský), katerina.mamulova.kutlakova@vsb.cz (K.M. Kutláková), sona.studentova@vsb.cz (S. Študentová), grazyna.simha@vsb.cz (G.S. Martynková).

http://dx.doi.org/10.1016/j.jhazmat.2014.01.059

[1]. Due this fact, ongoing research aimed to human protection against CWA and BWA is still of great importance.

There are many research studies, manuals as well as patents aimed at capturing and disposing of CWA and BWA. These methods are based on sorption, catalysis or chemical reactions [3–12]. However, decontamination and disinfection only deal with reduction of the effects of agent use. An important part of the research should be focused on prevention of injuries; for instance to develop materials which are able to effectively capture pervasive CWA or BWA and simultaneously prevent secondary contamination due to toxic compound release from material. Such material can be consequently used as personal protection clothing. One of the possibilities is polymer-clay hybrid microcomposites or nanocomposites that are known to have improved physical and mechanical characteristics including decreased gas permeability [13–15].

Yperite as one of the most significant CWA representative is often used for testing of resistance of polymeric barrier materials such as rubber, foils and protective materials because it easily penetrates through them [9]. Yperite or mustard gas (bis[2-chloroethyl]sulphide) is well known vesicant agent. This sulphur-containing organic substance is a highly reactive bifunctional compound with antimitotic, mutagenic, teratogenic, cytotoxic and carcinogenic properties. It is characterized by high toxicity, extreme multiple effects, high boiling point, high density and vapour pressure, high chemical stability, lipophility and penetration capacity [16]. It is an alkylating agent that, when absorbed, causes chemical reactions with cellular components resulting in cytotoxic effects [17]. Several studies after World War I and the Iraq–Iran conflict provided much detailed information about the long-term effects of yperite. The first symptoms can occur immediately or from several hours to days after exposure. Severe damages to the eyes, respiratory system, internal organs and skin are caused; the effects are related to dose and time of exposure [17,18]. It persists for a long period in temperate climates. There is no effective treatment against yperite intoxication. One of the possibilities is the wearing of protective clothing during decontamination or other contact [17].

Biological agents can be microorganism and toxins which are intended for use in military operations in order to kill, seriously injure or incapacitate exposed individuals by exerting their physiological effects [1]. A large number of biological agents have been investigated for their potential utilization as biological agents. Several bacterial strain such as *Bacillus anthracis* (Anthrax), *Y. pestis* (Plague), *Francisella tularensis* (Tularemia), *Brucella* spp. (Brucellosis) and *Malleomyces pseudomallei* (Melioidosis) have been ranged among most serious hazards.

Modified clay minerals are well known to have the ability to adsorb natural and anthropogenic toxic compounds [19–22]. Montmorillonite and vermiculite are two important clay mineral representatives. Both are ranged into phyllosilicates 2:1 characterized with layered structures and negative charge on the layers, which is compensated by inorganic cations such as Na^+, K^+, Ca^{2+}, Mg^{2+} in the interlayer space. In their natural form they are hydrophilic. Due to simple ion exchange of inorganic cations for organic cations they become hydrophobic and can interact with organic compounds. The utilization of hexadecyltrimethylammonium (HDTMA) and hexadecylpyridinium (HDP) cations for this ion exchange is well known. Both cations are members of the quaternary ammonium salt group, which share a positively charged hydrophilic ammonium moiety and long hydrocarbon hydrophobic chain. The compounds have bacteriostatic and bactericidal activity, which is due to their abilities to alter the permeability of cellular membranes allowing intracellular low molecular-weight components to diffuse out [19,22]. This process results in cellular death. While natural montmorillonite and vermiculite or their Na form showed no antibacterial effects, organically modified montmorillonites and vermiculite are efficient materials against selected bacteria such *Escherichia coli*, *Enterococcus faecium*, *Pseudomonas aeruginosa*, *Salmonella enteritidis* as was described in several research works [19,22,23].

The aim of the study was to prepare an effective barrier that will have a sufficient breakthrough detection time for a CWA such as yperite, and will simultaneously prevent secondary contamination as a consequence of yperite release from the barrier. The prepared material could be used as a protective cloth material. The effective barrier was prepared from a low-density polyethylene foil (LDPE) with modified clay minerals as fillers using montmorillonite and vermiculite in their monoionic Na and organically modified HDTMA and HDP forms. The breakthrough detection time (BT), permeation rates (F), an estimation of yperite capture in material (A) and total quantities of yperite penetration through the barrier systems (Q_p) were determined for all prepared materials by use of chemical indication tests and dynamic gas chromatographic methods.

Modified clay minerals were tested on antibacterial activities against potential biological agents such as *Y. pestis* and *B. anthracis* and other pathogenic bacteria *Staphylococcus aureus*, *Streptococcus agalactiae*, *E. coli* and *P. aeruginosa* which could be disposed on a protective clothing surface.

2. Experimental

2.1. Materials

Natural Ca-montmorillonite from a deposit in Ivančice (Czech Republic) and Mg-vermiculite from Brazil (supplied from Grena a.s., Czech Republic) with particle size smaller than 40 μm were used for preparation of modified clay minerals. Their crystallochemical formulas $(Si_{7.96}Al_{0.04})$ $(Al_{2.52}FeMg_{0.90}Ti_{0.04})$ $O_{20}(OH)_4(Ca_{0.24}K_{0.06}Na_{0.09}Mg_{0.10})$ and $(Si_{6.32}\ Al_{1.58}\ Ti_{0.1})$ $(Mg_{4.75}$ $Ca_{0.34}\ Fe_{0.91})$ $O_{20}(OH)_4$ $(Ca_{0.04}\ K_{0.38})$ were calculated on the basis of the elemental analysis using X-ray Fluorescence Spectrometry methods. The cation exchange capacities (CEC) of montmorillonite and vermiculite were 86 and 122 cmol(+)/kg, respectively, both

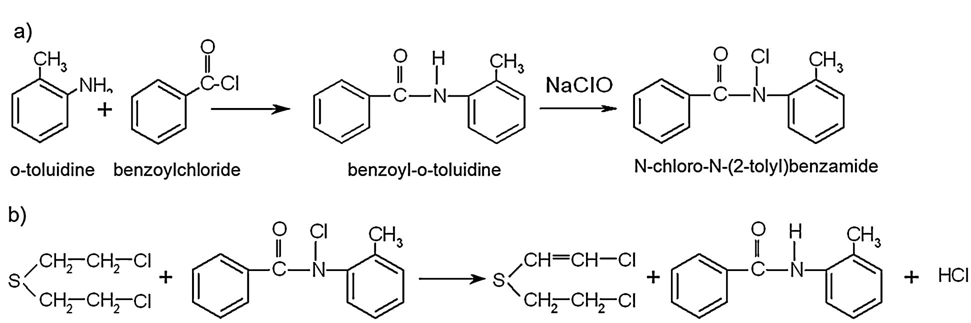

Fig. 1. Reaction scheme of a) N-chloro-N-(2-tolyl) benzamide preparation, b) yperite interaction with N-chloro-N-(2-tolyl) benzamide [25].