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Military practices and experiences and their effects on the environment

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Abstract

International humanitarian law (IHL) is signified as the bedrock rule for governing the term "Warfare" and their related risks. IHL is responsible of governing prohibition and restrictions on some specific weapons as well as methods of warfare as a part of a larger set of standards. This investigation is describing the current state of knowledge of the sulfur emissions from the warfare and leaking for the soil, marine environment and air. Throughout the entire work, bibliometric analysis as a significant tool to analyze the literature is conducted to evaluate the literature dealing with the sulphur mustard and its use in weapon welfare as a chemical weapon. The analysis is based on the literature cited in the field and the co-author occurrence. In such study, the collected existing toxicological effects of sulphur mustard and its listed derivatives are illustrated. However, a deficiency in information on the toxicity of some derivatives of such sulphur compound including 1-oxa-4,5-dithiepane and 1,2,5 – trithiepane which is required for concern. Finally, natural clay is examined as a non-toxic and eco- friendly adsorbent for sulphide removal from marine life. The experimental investigation is highlighted and studying the adsorption parameters optimizes the removal efficiency. the highest adsorption capacity revealed the acidic pH is favorable and using 1.5 g-clay/L is sufficient for removal.

Keywords: Classifcation, Distributed Denial of Service, Military; Warfare; International humanitarian law (IHL); Sulphur; Environmental concerns; Chemical weapons; Bibliometric analysis

1. Introduction

Catastrophic effects into the environment are attained through the intentional destruction from warfare. The terrible outcomes are not only disturbs the human, but also affects in ecological terms and may endure on the environmental natural resources. Weapons could be nuclear, biological and chemical tools. However, the chemical inevitable to generate huge consequences pollution into the environment since they cause a posing threat to humanoid, plants and animals lifecycle [1].

Globally, it is argued the most appropriate technique to address the concern is not via the environmental protection measures, but rather under positive consequences through the international criminal law. Thereby, those who deliberately target the environment during armed conflict can be signified as criminally liable. Over the past eras, the international criminal law has been developed in a quick manner. Thus, international efforts have been addressed to prevent the use of such toxic chemicals in land warfare. The initial action is begun in the nineteen centuries through the first attempt that regulates the use of weapons. Prohibition against poison or poisoned arms are including the international restrictive agreement for the usage of such weapons [2, 3].

Chemical warfare that is named "chemical weapons" could be categorized as a mass destruction arms. Chemical weapons is termed according to the international humanitarian law (IHL) as any chemical including toxic chemicals or may be their precursors that are applied to cause intentional death or harm from their toxic characteristics. Additionally, may be any equipment that is designed to weaponries such substances, which is also categorized under the definition of chemical weapons. Further, chemical weapons is indiscriminate in nature since they generate lifelong damage which is persists even after the end of the conflict and affects both humanoid and the natural environment. The prohibition of such chemical warfare through the organizations for the prohibition of the chemical weapons is a must and is probably amongst the supreme ancient ones in IHL [4-6].

During the military conflict, historically, many deliberate acts directed in destroying the natural resources and environment through the military conflict. International humanitarian law (IHL) that is a part of public international law has been devoted for setting rules for humanitarian reasons in order to border the armed conflict effects. Such IHL target is to protect people who are not dynamically participating in hostilities and forces boundaries on the methods and techniques of warfare. IHL regulates the behavior of parties once it has started [5].

Sulphur is signified as one of the elements in the periodic table. Whereas, although their naturally occurrence, it might possess an alarming environmental consequence in specific scenarios according to the Environmental Protection Agency (EPA) records. When sulphur-containing substances, i.e. fossil fuels are burned, the element reacts with oxygen to create a sulphur dioxide chemical compound that is a toxic gas causes a threat to both environmental and human health. Furthermore, acid rain that is mainly constituent of sulphuric acid release into the

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atmosphere can cause major damage to forests, agricultural crops, waterways and other habitats. Sulphur oxides might react with the atmospheric compounds and leading to form fine particulate matter that could affect the visibility leading to a sunlight blocking. Thus, this might act on animal and plants growth. Hence, this air pollution is leading to a serious damage to the human lungs and respiratory system. However, more information is still essential on the environmental and human health effects of chemical warfare to manage their future challenges. Policymakers are ongoing to make action and take steps to such emissions [7, 8].

In the current study the current toxicological and ecotoxicological data of the causes of sulphur products caused from the release of sulphur mustard into the environment and formed as an active source of mustard gas. Such sulphur compounds classifications are attained together with physical and chemical characteristics of such substances. Ecotoxicological data signified such compounds as toxic to aquatic organisms [7-9]. After the war, leading the chemical weapons into the environment is an issue. Historical available data on the use of mustard gas as a chemical warfare is essential, which is further provide the presence of sulphur derivatives and transformation products in the environment. However, with the lack of knowledge, such materials deposition into the nature and the ecosystem are often leaving to be reclaimed by nature. Also, due to their dangerous characteristics some places are left with limited access.

Herein, this research paper is drawing an attention to the exposures and toxicities of the sulphur mustard and the available and gaps data for their use as a used chemical warfare agents. This research is highlighting the concern and toxicity such substance.

2. Bibliometric Analysis

Presently, with modern research items, analyzing data in a specific field and topic in a visualized schemes is conducted through bibliometric analyses. Such tool can act as a mapping key aspect to illustrate the most cited items in the field of mustard gas and sulphur compounds and their related terms in the field of weapons and warfare. GoogleScholar platform is applied as a search to provide the cumulative data of literature cited in the field of “Mustard gas”, “Sulphur derivatives”, “Warfare” AND “Weapons” the attained data are exhibited in Fig. 1. The research articles in such keywords are explored and offered as annual cumulative research published articles, reviews, editorial material and letter. Commonly, the number of the research cited articles usually is in increase to reach a satisfied reasonable result. However, according to the data in Fig. 1, not so much published data in the research articles available in the literature. A concise outline of the investigated research conducted is the review articles that are popularly represents this field according to the Fig. 1 (sub-plot).

Thereby, to show the state-of-the-art figure of the sulphur mustard, the research survey analysis was carried out on the Web of Science platform. The search items were "Sulphur mustard AND Weapons”. Consequently, the results attained from the "Web of Science Core Collection" database and the VOSviewer software (version 1.6.16.0) was obtained via the time-period of 2000 to July 2024. The data is designated for the object of analyzing the research articles’ keywords and then design the map analysis integrates a network. Afterwards, the

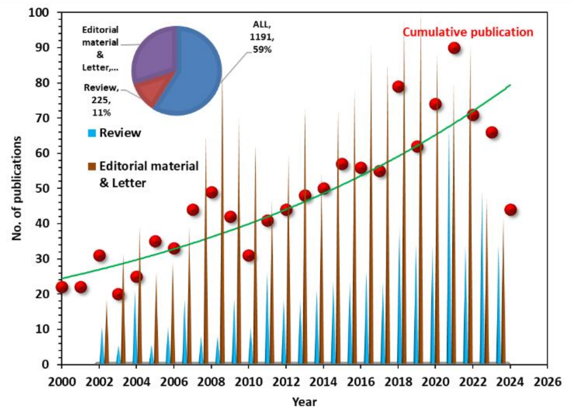

Figure. 1. Compared publications on the sulphur mustard publication related to weapons from 2000 to 2024. Source for “Mustard gas”, “Sulphur derivatives”, “Warfare” AND “Weapons” cases data: www.googlescolar.com (Accessed on 30 July 2024)

overlay and density image mapping are proposed from the VOSviewer software. Commonly, the current search is based on the co-occurrence associated with authors' keywords and is investigated according to the minimum number of such keyword's occurrence. Accordingly, the parameters are regulated in the software, followed by the map designing through the common VOSviewer report that is signified as overlay visualizations to label density visualization over periods. The achieved data the cited research papers linked to the Sulhpur mustard research represented as the bibliometric mapping clusters as displayed in the Fig. 2. The hotspots clusters might be validating the intensive research studies based on the analyzed data reported via the data from “Web of Science” core collection from the search terms “TI is (Sulphur mustard AND Weapons)”.

3. Analysis of Authors and Research Collaborations

To highlight a more implication on the frontiers in the subject of sulphur mustard weapons, a bibliometric analysis for the leading investigators or group of researchers for the most creative scientists in the topic is conducted via the use of VOSviewer software is exhibited and displayed in Fig. 3. Cluster and label size controls the weight of the item and the leader researcher contribution. Consequently, the superior the

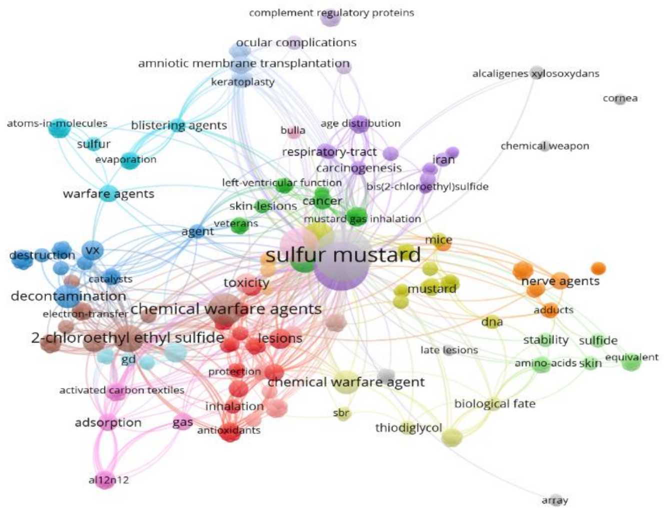

Figure. 2 Key terms occurrences network visualization map in Sulphur Mustard publication related to weapon warfare

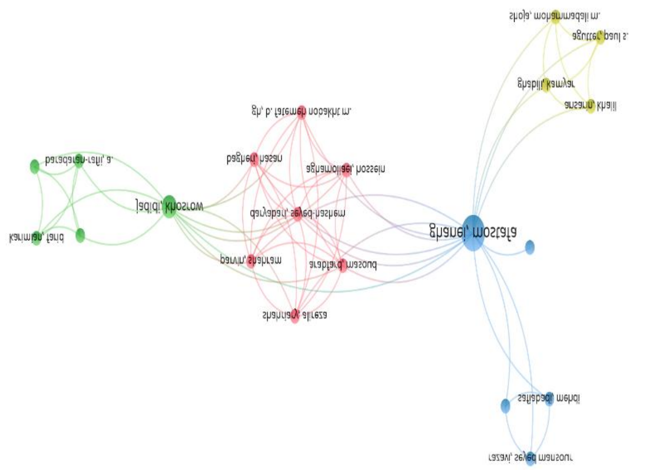

Figure.3. Bibliometric network mapping generated via VOSviewer. A. Network map showing the collaborations between authors and the citation authors through the Co-authorship overlap visualization map for Sulphur mustard AND Weapons

weight of the researcher, the greater the item's label and circle as displayed. The information in Fig. 3 follows the research papers by the main authors. The mapping indicates the most strength authors are Mostafa, Khosrw, Rafil, Farid and their co-workers, who are principally focused to sulphur mustard as a weapon warfare. However, it is notable that less work is conducted in such field which essential work is still required.

4. Sulphur Mustard Source and Occurrence

Although sulfur is an essential element, it possesses some negative impacts on terrestrial and aquatic ecosystems. The sulfur cycle is closely linked to carbon, nitrogen, phosphorus, and iron cycles. Also, it may affect on all environmental compartments. The main sulphur presence is illustrated in Fig. 4. According to the data in Fig. 4, the global main reservoirs of sulfur component is in its global cycle are in the form of sulfates. Such sulfates are dissolved in marine waters, sulfates bound in evaporates, and sulfides in classic marine sediments. Sulfur compounds present in the atmosphere, biosphere, and the terrestrial part of the hydrosphere constitute a much smaller portion of the total cycled sulfur [10-12].

Initially, Sulphur mustard, that is a human-made and signified as a major chemical warfare agent is synthesized in 1822 by Desprets, then in 1860 by Nieman and Gutherie. Its first use was during World War I, however, its last application was in the war between Iran and Iraq [1, 13]. In such war, Iran-Iraq war, the injured of Iranians was reached to more than 100,000 and one-third of them are still suffering from its long-term effects. Sulphur mustard is categorized as "blistering agent" and named as "mustard gas", "mustard agent," or according to the military designation is known as "H" or "HD". It might be existed in clear to yellow or brown color when it is in liquid or solid form. Sulphur mustard is an alkylating agent causes a severe damage to humans that including ocular and dermal injury causes blistering of skin and mucous membranes. Also, it can cause severe problems in respiratory, reproductive toxicity, gastrointestinal effects, hematological effects, cancer disease and eventually cell death [2, 3]. Such substance might be smelled such as garlic, onions, or mustard smell. However, sometimes it may possess no perceivable odor. Sulphur mustard could be in a gas vapor, oily textured liquid or a solid. At room temperature, it is usually a liquid. Sulfur mustard is usually a solid when the temperature is less than 58° Fahrenheit. After a release of sulfur mustard into the air, humans might be exposed via skin or may be eye contact, or it might be breathed resulting in early and late toxic effects and respiratory problems [14-18].

Sulphur mustard also, could be released into the watercourse and thereafter it could be reached to humanoid through touching or drinking such water contaminated with sulfur mustard. However, Sulfur mustard may be represented in the form of to liquid sulfur mustard by swallowing sulfur mustard which leading to a skin or eye problems [19]. Sulfur mustard could contaminate food through flowing into it from soil or water that reached further to people through eating, drinking or even touching food contaminated with such toxic substance. Furthermore, inhaling sulfur mustard vapor that may be contaminating clothes can also reach to humans. Since, sulfur mustard vapor is heavier than air, this makes it sinking into low-lying areas, which increase its toxic risk of exposure. In the mild and normal weather conditions, sulfur mustard can remain from one to couple of days in the in the environment. But it might last for weeks in the very cold circumstances this makes it is more toxic for remaining for long term in the cold weather places [20, 21].

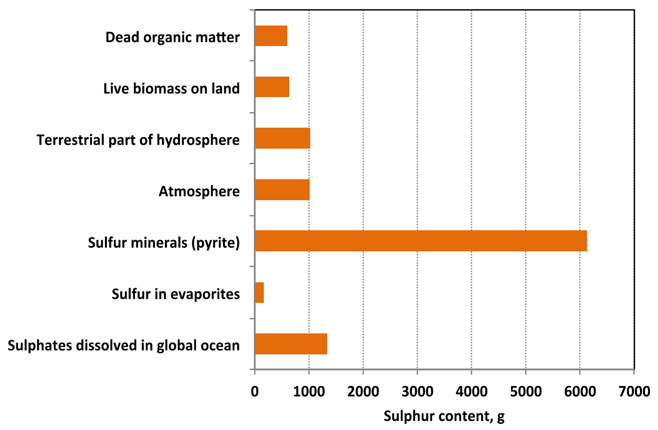

Figure. 4. Sulfur content in specific environmental compartments

5. Toxicity and Long-Term Health Effects of Sulphur Mustard

For approximation of ten years, sulphur mustard and comparable bifunctional chemical agents have been applied as chemical weapon in warfare. Sulphur mustard is very lipophilic and thereby can penetrate epithelial tissues easily. Hence, at high doses of exposure, victims exposed to such sulphur mustard material could be exposed for death even in few hours or weeks. But, the low doses of exposure cause both acute injury to the eyes, skin, respiratory tract and other parts of the body, and chronic sequelae in these organs are often debilitating and have a serious impact on quality of life [5]. Sulphur mustard amount and the length exposure time are affecting its signs and symptoms. Thus, the persons are exposed into sulfur mustard is differs in complications of exposure. Also, such signs and symptoms might be occurring immediately, but it takes about one day to appear. Sulphur mustard is absorbed by inhalation though the skin exposure or by gastrointestinal tract, thereby, it undertakes intramolecular cyclization to form an intermediate ion that is named ethylene episulfonium. Such ion in turn reacts with and alkylates nucleic acid and proteins, resulting in impaired cell homeostasis and eventually cell death [3, 22]. Typically, sulphur might possess specific effects on body parts including skin since it might blistering of skin into yellow in color, pain, itching, skin redness and bloody nose. Stomach pain and respiratory problems and cough. Diminished formation of blood cells and might also reduce both the red and white blood cells that is leading to weakness, bleeding, and other infections such as diarrhea, nausea, runny nose, vomiting and fever. Eye also is severely affected with sulfur mustard and cause eye pain; eye could be irritated eye tear, temporary blindness. However, the exposure to high doses reached to convulsions, light sensitivity, insomnia, permanent or temporary blindness and or temporary or permanent eye injury or chronic eye infections. Respiratory failure is also might reach to death. Skin that exposed to high doses of sulphur mustard reached to second- and third-degree burns, skin scarring, pigment changes, and might reach to a skin cancer. Inhalation may result in loss of taste and smell, chronic respiratory disease, recurrent respiratory infections, and possibly respiratory cancers [23].

Extremely heavy exposure to sulfur mustard might cause central nervous system excitation that is cause to convulsions in animals. However, in some wars the data revealed that the effects may be mild and very non-specific neurologic including headache, anxiety, fear of the future, restlessness, confusion and lethargy.

6. Sulphur Mustard Methods of Detection in the Environment

Chemical weapons warfare is signified as inevitable threat. Such damage associated to both soldiers and civilians since it may attack accidently thousands of humans as well as other people may be contaminated. In this concept, equal concerns to its strict control and proper decontamination are essential. In this regard, a special concern to locate sulfur mustard that contaminating surfaces using a water-based sprayable polymer containing a sulfur mustard fluorescent probe is previously located. In such technique, immobilizing the probe in a water-soluble polymer developed a sprayable material. Such method could enable the localization of sulphur in contaminated places which is detectible by the naked eye. Such method possesses the merit of a nondestructive method since it is not necessitating damage to the surface of interest.

However, there are primary methods of sulfur mustard analysis in the environment. For example, a colorimetric assay utilizing 4-(p-nitrobenzyl) pyridine that is also frequently applied and used for detection. However, Gas chromatography and mass spectroscopy (GC/MS) is more commonly used for detecting sulfur mustard. thin-layer chromatography (TLC) with a colorimetric followed by detection with a 4-(p-nitrobenzyl) pyridine detection system has been qualitatively and quantitatively used and showed a useful result in detecting water, soil and plants with a detection limit of 1 μg/sample spot [5, 24].

7. Sulphur Mustard and Its Degradation Products

According to the literature reviewed, the data available for sulphur mustard degradation and its derivatives are still limited. As the sulphur mustard is a strong carcinogen, thus the toxicity and genotoxicity and carcinogenicity of the compounds should be highlighted and investigated. Hence, the measured environmental toxicity of the detected degradation products of sulphur mustard is recorded. The presented mustard gas derivatives are displayed in Table 1 and their toxicity is displayed in the Table (1), which is varied from genetic toxicity and toxic derivatives [25].

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Table 1. Measured toxicity data profile of mustard gas and its degradation products

Compound	Toxicity
mustard gas	lung problems
thiodiglycol	Sub-chronic
1,4 – dithiane	no significant mutagenic effects.
1,4 – oxathiane	negative results
1- oxa-4,5-dithiepane	not available
1,2,5- trithiepane	not available

8. Experimental Investigation "Sulphur Treatment from Wastewater"

8.1 Methodology

Clay that is naturally occurred was collected from the eastern desert in Egypt and introduced to be the adsorbent material. Initially, for the object of removing any moisture content from the clay, it is as received is subjected for oven drying 105°C for one week time prior to ball mill grinding to attain a fine powder. In order to prepare the simulated adsorbate solution, a synthetic solution of sulphur contaminating water was synthetically prepared to be a simulated sulphur containing wastewater in the form of sulfide. A stock solution is prepared then varied concentrations are thereafter prepared ranged from 50 to 400 mg/L and subjected for treatment.To assess the adsorption capacity of such suggested clay substance as an adsorbent, batch tests were explored at 298 K. A prepared solution of 50 mL of sulfide was poured into various containers and sealed to be exposed for mixing to investigate the isotherm time. Then, when the contact time is determined further parameters are investigated such as effect of pH, adsorbent dose and concentration of the pollutant to be optimized. Subsequently, the remaining sulfide is investigated through the application of chemical oxygen demand according to the standard methods. The schematic graphical illustration of such process is exhibited in Fig. 5.

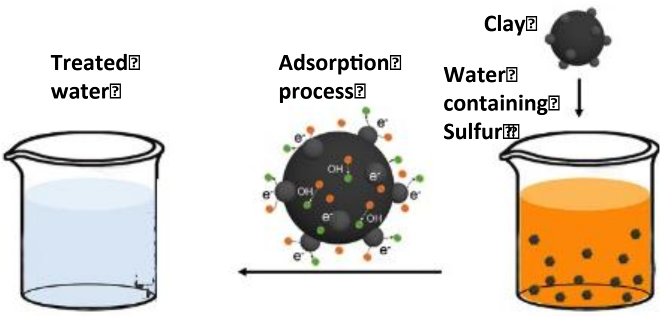

Figure. 5. Schematic representation of the adsorption process

8.2 Clay Characterization

Fourier transform infrared (FTIR) spectrum is applied as significant tool to distinguish the different forms of minerals existing in the clay. FTIR analysis and the data is exhibited in Fig. 6. There are a main absorption intensive bands for clay such as the band at 781.9 cm^{-1} that is signifying the (O-H) stretching vibration. The silanol (Si–O) bad is identified at identified at 462.8 cm^{-1}, 530.5 cm^{-1}, 801.7 cm^{-1} and 1025.3 cm^{-1} stretching that are confirming the presence of silica in the clay. Also, the band appear at 10223.5 cm^{-1} also verified the occurrence of quartz [26]. However, the vibrating bands at 527.3 cm^{-1}, 1626.1 cm^{-1}, 3503.2 cm^{-1} and 3673.5 cm^{-1} indicate the possibility of the hydroxyl linkage [27].

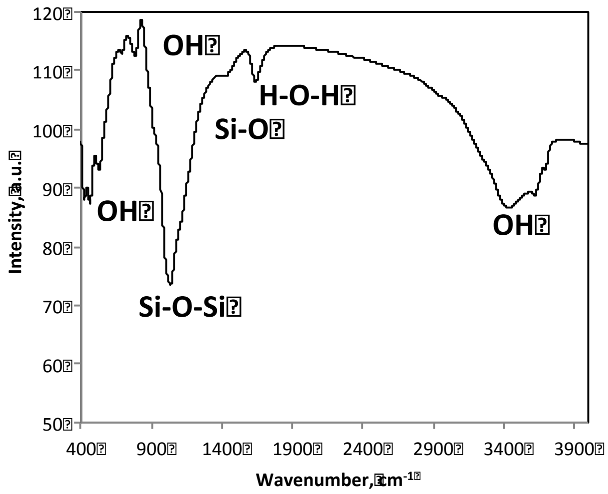

Figure. 6. FTIR spectrum of the adsorbent clay

In order to examine the structure of such adsorbent material, the clay is characterized using scanning electron microscope (SEM). Such image showed irregular layered structure that possess a semi smoothed like surface. The surface displayed agglomerated particles with irregular shape according to the morphology displayed in Fig. 7.

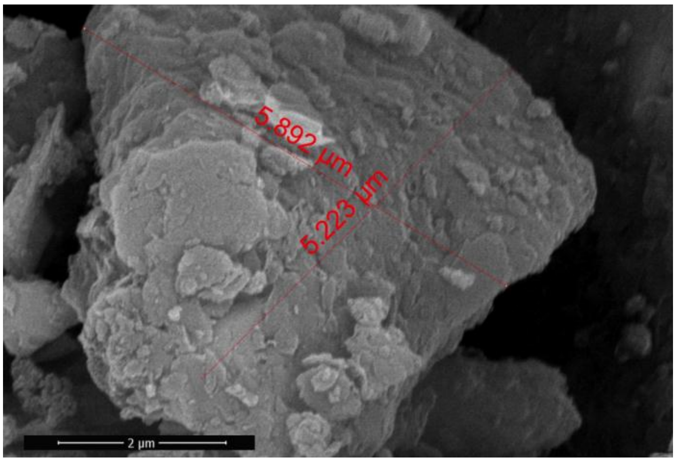

Figure. 7. Morphological structure of clay adsorbent

8.3 Adsorption Process

Primarily, the contact time of equilibrium for the adsorption methodology is assessed according to changing the contact to establish the adsorption matrix. The adsorption isotherm time is graphically represented in Fig. 8 (a). The results revealed that the adsorption equilibrium was recognised at 1.5 hr of contact time between the aqueous sulphide solution and the clay adsorbent. Subsequently, however, no further change in the adsorption system with the time prolonging. This might be approved by the saturation of the adsorption sites of the clay material with the pollutant. But, rapid adsorption in the initial stage that is signified as a high adsorption rate could be associated to the high initial concentration of the pollutant on the adsorbate and the available vacant sites on the clay adsorbent [28].

Furthermore, to evaluate the full adsorption matrix, the initial pollutant concentration should be evaluated. In this regard, at 1.5 hr at 298 K using 0.1 g of clay, the adsorption process is conducted by changing the sulphide dose and the results is displayed in Fig. 8 (b). Notably, the results showed that an increase in the sulphide results in a noteworthy progress in the adsorption capacity. This positive relationship signifies the adsorption capacity could be further improved by continue increasing the pollutant concentration. The adsorption capacity increases from 1.0 to 2.5 mg/g with increasing the pollutant concentration from 50 to 400 mg/L, respectively. but further increase declines the adsorption capacity [29].

The influence of different doses of clay material is represented in Fig. 8 (c) and the maximal adsorption capacity is corresponding the use of 1.5 g/L of clay. Although, extra increase in clay more than such dose is declines the adsorption process. This might be attributed to the role of clay is a reversible effect since it agglomerated together and thereby the surface area is declined rather than increases. Thus, results in a decline in the sportive surface available for adsorption [30].

pH effect plays is crucial role in adsorption systems. In this concept, its effect on such matrix is investigated by varying the pH from the acidic to alkaline circumstances. Since, the pH is controlling the surface charge of both adsorbent/adsorbate. The initial contaminated wastewater with sulphide is ranged in pH from 2.0 to 8.0 is exhibited in Fig. 8 (d).

Notably, upsurge in the pH value, a diminution in the adsorption capacity is attained. This might be attribute with, the low pH value (2.0), the surface of the clay adsorbent is positively charged. Si-O (silanol) active group on the clay surface are surrounded by hydronium ions and that is thereby protonated since the presence of H^+ in the medium in excess. Thus, blocking the metal ions from binding sites on the clay adsorbent and this is not favour for the positively charged sulphide adsorption. Nevertheless, by increasing the solution pH, the deprotonation mechanism of the active groups is occurred and this attributed to a decrease in the number of positively charged sites on the clay adsorbent. Hence, overall, such capacity is declined with the pH increase [31-33].

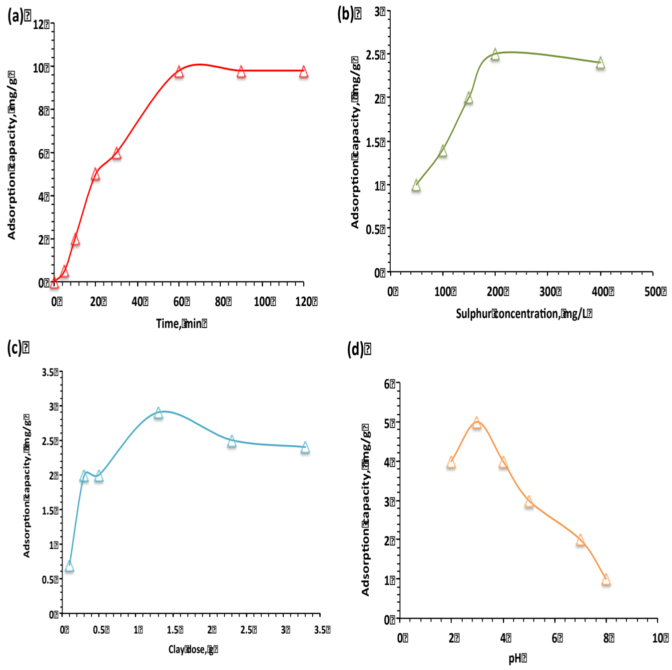

Figure.8. Effect of adsorption isotherm and process parameters on adsorption capacity (a) adsorption time, (b) pollutant concentration, (c) adsorbent dose and (d) pH influence

Conclusion

Scientific and technological uncertainties should be clearly stated for the chemical weapons. The widespread use of such substance, sulfur mustard, in the warfare in the past century has proved its high long-lasting toxic effects on both environment and humanoid. Further, future military conflicts and rules should be conducted. Its long-term effects might affect on eyes, skin, respiratory and neurological system and the are the major targets for military purposes. A comparison between the long- and short-term effects are highlighted through such investigation. Based on these summarized results available about sulphur mustard and its occurrence as well their toxic effects on the creatures, it is concluded that further assessment is essential and further toxicity data need to be produced. Hence, chemical weapons required to be signified separately and response strategies must be knowledgeable by the technical and scientific essentials. Also, better understanding of chemical weapon and their destruction issues linked to them is required to be provided. Furthermore, for a viable solution of sulphur in the marine life a suggested sustainable solution is suggested to remove sulphur material from wastewater. The experimental data revealed that clay could be valuable opportunity to remove sulphide from wastewater. The experimental results verified the isotherm time is reached at 1.5 min and increasing the adsorbent dose up to 1.5 g-clay/L is viable for removal and the acidic pH is essential.

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