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Feasibility study for application of the marine coral powder as a novel adsorbent for Volatile Organic Hydrocarbons

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ABSTRACT
The marine coral has a porous outer surface and it has served in the processes such as water treatment systems, removal of carbon dioxide and adsorption of arsenic. Based on the need for cheap and efficient adsorbents, in sampling, the aim of this study, comparison of the efficiency of marine coral powder and activated charcoal in adsorption of volatile organic hydrocarbons was considered. In this experimental research, a certain concentrations of 8 volatile organic hydrocarbons: (para-Xylene, Chloroform, Carbon tetrachloride, tert-Butanol, Pyridine, Acetone, Ethyl acetate and Diethyl ether) was injected into dynamic atmospheric chamber in the NTP (Normal Temperature and Pressure) conditions. Air sampling was performed with the tube containing marine coral powder as well as the tube of activated charcoal, based on the standard method of NIOSH (National Institute of Occupational Safety and Health) and in the same laboratory conditions. Then samples were injected into the gas Chromatograph apparatus and analytical comparison has been done between the amount of adsorption of hydrocarbons by activated charcoal and coral powder-test and Mann-Whitney were done with SPSS V.20.Findings showed that there was a significant difference between the amount of adsorption of Para-Xylene, carbon tetrachloride, tert-Butanol, Pyridine, acetone and Ethyl acetate hydrocarbons by activated charcoal and coral powder ($P<0.05$(. The amount of hydrocarbons adsorption by activated charcoal was, more than coral powder significantly ($P<0.001$). Based on the present research, in sampling of used hydrocarbons, the marine coral powder was less efficient than the activated charcoal, and it is recommended that more works be designed about other techniques such as coating of the marine coral powder in order to the improvement of adsorption capacity for volatile organic hydrocarbons.
Key words: Marine Coral; Novel Adsorbent; Air Sampling; VOCs

INTRODUCTION
Nowadays, thousands of hazardous materials with different properties exist in the workplace that is important for health and safety of the workers [1]. Based on this fact, air pollution has been increased mainly due to the hazardous compounds present in the effluents emanating from industries. Hydrocarbons as an occupational pollutant have great industrial importance, and are the most important ingredients of natural gases, petroleum and tar. These materials are employed in chemical industries as fuel, softeners, solvents, building and raw materials. Gaseous hydrocarbons can be suffocating agent (as air substitute), hypnotic materials (sleep-inducing) and weak narcotics. Contact with liquid hydrocarbons leads mostly to skin disorders like dermatitis, and some of the aromatic hydrocarbons compounds have carcinogenic properties [2].
In order to the assessment of air pollution in the workplace and prediction of the possible risks, it is essential to accurately determine the type and the amount of air pollutants [1].Quantitative survey air sampling and assessment of the pollutants are the most important thing of the workplace. In order to air pollution control in the workplace, the main part of the process of air sampling, is data collection for decision making about methods of control [3]. Activated charcoal is the most important and widely used material for detection of gases and vapors [4]. Activated charcoal is a nonpolar substance, and thus it is regarded as an excellent sorbent for organic vapors. This sorbent, due to its porous structure and a relatively high surface to

weight ratio, is considered as a suitable adsorbent [5].

For many years, the coral reefs and their structural simulations are used as reagents of metals due to their sensitivity to the chemical and physical changes [6]. In 1975, fossilized coral limestone was used in the water filtration systems [7]. In Maeda study, it was used 3-ferric hydroxide filled with coral limestone as a selective adsorbent for penta-valent arsenic ion and as an adsorbent for tri-valence and penta-valence arsenic in aqueous environments [6, 8]. And also in Ohki study, this substance was used as arsenic adsorbent. In both studies, the arsenic adsorption ability was less than activated charcoal [9]. In Karimian study, elimination efficiency of the colors including 5-R cyanine acid and 3-R reactive orange by coral limestone and Lica granule in the aqueous environment was done and the results indicated that the using of the coral limestone and Lica granule due to its proper density, rapid sedimentation, easy production and low cost can be a proper choice in color removal from wastewaters [10]. According to the porous peripheral surface of the marine coral and its application in water treatment as well as, in removal of CO_2 and arsenic adsorption, it is expected that it can be used as suitable adsorbent in sampling of some air pollutants [7, 11].Based on the geographical situation of Iran, with corals coasts and increasing demand for new adsorbents in the view points of cost, adsorption efficiency and availability for sampling of pollutants besides to common adsorbents, such as activated charcoal adsorbent, this study for feasibility study and evaluating of the efficiency of marine coral powders as adsorbent for eight volatile organic hydrocarbons in comparison with activated charcoal adsorbent was designed.

MATERIALS AND METHODS

This research was designed as an experimental study in the NTP conditions. To prepare a predetermined airflow, an air compressor with a dehumidifier filter was used. To achieve this, a standard gas generating device with a flow through the sampling chamber was constructed to provide a wide range of concentrations [12-14]. The sampling set (Fig. 1) included as follows: dry gas meter, syringe pump, the standard dynamic chamber, adsorbent tubes, adsorbents holders and finally low flow personal sampling pump.

All chemicals were purchased from MERCK Company. For providing a known concentration of gaseous analytes in the desired range, a dynamic atmosphere producer system was used (Fig. 1/Table 1).

The marine corals were obtained from the south coasts of Iran. In order to the marine coral pretreatment, washing with methanol (3 times) and heating (1h; 70^{oC}) to evaporate water, pollution elimination and pore expansion were used. Then massive marine coral were ground and sieved through a 20/40mesh screen. 0.15g marine coral was packed at a glass tube similar to charcoal tube (7 cm L, 4mm ID.) followed by end capping with holders (Fig.2).

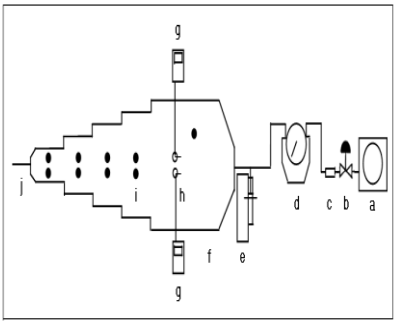

Fig.1: The schematic of the sampling set

a: Compressor, b: Pressure regulator, c: Dehumidifier filter, d: Dry gas meter, e: Syringe pump, f: Standard dynamic chamber, g: Personal sampling pump, h: Chamber sorbent tubes site: Container caps, j: Chamber output

Table.1: Experimental Conditions in standard dynamic chamber

Temperature	20ºC
Humidity	a dehumidifier filter was used
Pressure	NTP conditions

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Fig.2: Sampling holders designed for dynamic chamber sampling

NIOSH standard methods for hydrocarbons sampling in the NTP conditions were used in this study by activated charcoals are as follows: 1501 for sampling of para-Xylene, 1003 for sampling of Chloroform and Carbon tetrachloride, 1400 for sampling of tert-Butanol, 1613 for sampling of Pyridine, 1300 for sampling of Acetone, 1457 for sampling of Ethyl acetate and 1610 for sampling of Diethyl ether.

For provision of the fixed and determined concentration within the chamber, at least 5 ml from practical solutions was injected to the interface pipe. Then, by using a personal sampling pump with a flow rate of 150 ml. per min., sampling of the hydrocarbons by activated charcoal adsorbent tube was performed as well as for tubes containing the marine coral powder, at the same time and same experimental conditions.

Based on the dynamic chamber design and in order to accuracy and contact surface enhancement of the air pollutants with adsorptive sites, holders was used and one-side the sorbent tube was placed inside the holder and the opened side of the tube was directed into the chamber horizontally in the direction of air current (Fig.3). Then air was performed by using of the low flow sampling pump in the same conditions for adsorbents (Fig. 4). Carbon disulphide (1 ml.) for 30 minutes was used in the sample preparation stage, and samples were injected into the gas chromatography apparatus (Model: UNICAM4600) (equipped with a Flame Ionization Detector (FID)) for three times. Apparatus Temperature Program was set as: detector temperature: 200$^{\circ C}$, the temperature at the injection site: 200$^{\circ C}$ and the initial column temperature: 50°C as well as a capillary column was used: RTX-1(Fused Silica) (30m long by 0.32 mm ID).Statistical comparison between the amount of hydrocarbons adsorbed by activated charcoal and coral powder was performed by T-test and Mann-Whitney tests finally.

Fig.3: Holders arrangement in the dynamic chamber

Fig.4: Air sampling train and adsorbent tubes arrangement followed by sampling holders

RESULTS AND DISCUSSION

In this study, 48 samples were prepared and tested as follows: 24 samples from marine coral powder and 24 others by activated charcoal. The mean adsorption capacity of the used hydrocarbons by activated charcoal and marine coral powder was obtained 50.87 and 1.53, respectively (Table 2).

Table2: Adsorption comparison between marine coral powder and activated charcoal for volatile organic hydrocarbons

VOCs	Adsorption rate		p-value
	Marine coral powder Mean±SD(median area)	**Activated Charcoal Mean±SD(median area)**	
Chloroform	3.36±0.15(3.4)	3.05±0.14(3.1)	0.05
Éthyle acetate	0	22.83±2.08(18.6)	0.037
para-Xylene	0	1.19±371(1.32)	0.037
Acetone	0	74.5±6.86(70.3)	0.037
Diethyl ether	8.56±4.04(10.7)	87.6±6.45(73.4)	0.05
tert-Butanol	0.3±0.53(0)	45.04±4.06(46.6)	0.046
Pyridine	0	30.73±2.17(22.0)	0.037
Carbon tetrachloride	0	24.03±1.43(17.9)	0.037
Total hydrocarbons	1.53±3.17	50.87±50.52	≤ 0.001

After injecting samples and analyzing them by gas chromatography apparatus, based on the Table2, there was a significant difference between the adsorption of hydrocarbons of para-Xylene hydrocarbons, Carbon Tetrachloride, Butanol, Pyridine, Acetone, and Ethyl Acetate by the activated charcoal and marine coral powder ($P<0.05$) and the amount of adsorption of hydrocarbons by activated charcoal, in total, was more than marine coral powder, significantly ($P<0.001$). In the other hands, the obtained results of this study showed that, in the same laboratory conditions, the mean adsorption of the used hydrocarbons by the activated charcoal was higher than marine coral powder and activated charcoal had better efficiency in adsorption of samples in comparison with the marine coral powder.

Analytical use of natural substances has been applied throughout human history for centuries [15]. Among the most commonly used natural products, especially in Iran is marine coral. Harper has introduced activated charcoal as one of the most common adsorbents for adsorption of volatile organic compounds due to the high porosity [16]. In Tang *et al*. study, activated charcoal tube has been used for sampling of volatile organic compounds [17]. In other studies, the activated charcoal was used in sampling of aromatic hydrocarbons such as Toluene and p-Xylene and the adsorption of these two compounds was consistent with the results of this study [18]. In Matysik *et al.* study, the adsorbent of activated charcoal was used for passive sampling of microbial volatile organic compounds [19]. In Haghighat *et al.* study, the adsorbent of activated charcoal was used to remove some volatile organic compounds such as Toluene and Ethyl Acetate in buildings that were ventilated mechanically and the adsorption of these two compounds was consistent with the results of this study [20]. The above-mentioned studies show that application of activated charcoal for the adsorption of volatile organic compounds is unique yet. Although activated charcoal is considered to be the most effective absorptive and adsorptive agent known but a progressive research exists for novelty in adsorbent with benefits such as native availability and price. Recently many researchers have been engaging in studying the removal of a variety of commonly used pollutants from waters and air by novel modified charcoal and other adsorbents [15, 21-28].

It seems that the outer calcareous shell of marine coral that contains mineral substance overcome to high porosity of marine coral outer surface, in sampling of volatile organic hydrocarbons compared with activated charcoal [5]. Based on the results of Ohki study, the ability of adsorption of arsenic by 3-ferric hydroxide filled with coral limestone was lower, two times, than activated charcoal that in this case, it is, to some extent, consistent with the results of this study [9].

CONCLUSION

Volatile organic compounds emit from a wide range of sources inside of industrial units and ambient air in urban areas [13] and are among the most important classes of toxic chemicals considering environmental and occupational health which can be quantified by several methods [12].According to the obtained results of this study, for sampling of used hydrocarbons, marine coral powder has lower efficiency than activated charcoal, thus, based on this fact that accessibility of it is high in Iran, and very lower cost of its preparing than activated charcoal, it is recommended that for improving of the quantitative and qualitative efficiency in adsorption of volatile organic hydrocarbons, more work be designed about other techniques such as multiwall carbon nanotube coating [29],spherical adsorbents synthesized from phosphorylated polymeric precursors [22], development of copper oxide nanoparticle for marine coral modification [25],synthesis of TiO_2/marine coral composites [30]in order to the improvement of the adsorption capacity of the marine coral powder for volatile organic hydrocarbons.

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ETHICAL ISSUES

Authors observed the Ethical issues such as plagiarism.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest in the research. All Financial source of the study was provided by Hamadan University of Medical Sciences.

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