

# Use of modified and petroleum -impregnated bentonite mulch as an eco-friendly stabilizer of wind erodible sands

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## Highlights

The capability of natural and modified [bentonites](#) to absorb petroleum studied.

Modified bentonite impregnated with petroleum was examined as a mulch.

The produced mulch protected its underlined sands against removal by wind (60 km/h) speed.

The produced mulch significantly prevented transfer of [PAHs](#) to drainage and runoff waters.

## Abstract

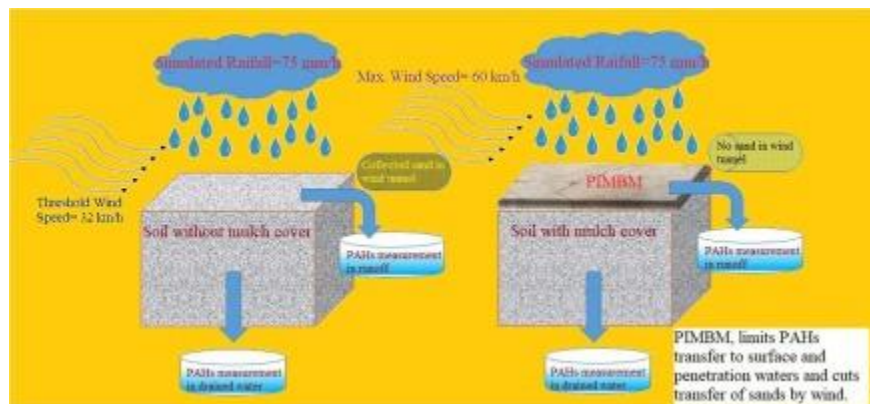
This study aimed to develop a method for the management of petroleum pollutants released into the environment using modified bentonite and to evaluate the use of petroleum-impregnated modified bentonite, as an eco-friendly and resistant mulch to stabilize mobile sands exposed to wind erosion. Bentonite was modified using hexa-decyl-tri-methyl-ammonium bromide to increase its capacity for petroleum adsorption. The resistivity to breakdown of the produced mulch was determined against wind, runoff, and by drainage water caused by simulated rainfall. Results showed that the basal spacing of the modified bentonite increased 162% compared to unmodified bentonite and it was able to adsorb petroleum, 5 times its base weight. The produced mulch was resistant against wind flows up to  $16.7 \text{ m s}^{-1}$  with no soil loss during 5 min, while the untreated sandy soil started to move at a threshold speed of  $10.3 \text{ m s}^{-1}$  (with a soil loss rate of  $53 \text{ g m}^{-2} \text{ s}^{-1}$ ) and the tray of soil was fully eroded after 135 s. Analysis of the drainage waters which passed through the mulch showed that mulch 2 (ratio 5:1, sandy soil: modified clay + unmodified clay (1:1) mixed by petroleum) retained more polycyclic aromatic hydrocarbons compounds,

compared to mulches 1 (ratio of 5:1 sandy soil: unmodified bentonite mixed with petroleum) and 3 (ratio 5:1:0.5, sandy soil: unmodified clay: modified clay mixed by petroleum). Analysis of the runoff water samples also showed that [PAHs](#) retention in mulch 2 is significantly higher than the amounts retained by mulches 1 and 3.

خلاصه:

این مطالعه با هدف توسعه روشی برای مدیریت آلاینده‌های نفتی آزاد شده در محیط زیست با استفاده از بنتونیت اصلاح‌شده و ارزیابی استفاده از بنتونیت اصلاح‌شده آغشته به نفت، به عنوان یک مالچ سازگار با محیط زیست و مقاوم برای تثبیت ماسه‌های روان در معرض فرسایش بادی انجام شد. بنتونیت با استفاده از هگزا-دسیل-تری-متیل-آمونیم بروماید اصلاح شد تا ظرفیت جذب نفت آن افزایش یابد. مقاومت مالچ تولید شده در برابر تجزیه در برابر باد، رواناب و آب زهکشی ناشی از بارندگی شبیه‌سازی شده تعیین شد. نتایج نشان داد که فاصله پایه بنتونیت اصلاح‌شده در مقایسه با بنتونیت اصلاح‌نشده ۱۶۲ درصد افزایش یافته و قادر به جذب نفت، ۵ برابر وزن پایه خود است. مالچ تولید شده در برابر جریان باد تا سرعت ۱۶.۷ متر بر ثانیه مقاوم بود و در طول ۵ دقیقه هیچ گونه هدررفت خاکی نداشت، در حالی که خاک ماسه ای تیمار نشده با سرعت آستانه ۱۰.۳ متر بر ثانیه (با نرخ هدررفت خاک ۵۳ گرم بر متر مربع بر ثانیه) شروع به حرکت کرد و سینی خاک پس از ۱۳۵ ثانیه کاملاً فرسایش یافت. تجزیه و تحلیل آب‌های زهکشی که از مالچ عبور کردند نشان داد که مالچ ۲ (نسبت ۵:۱، خاک شنی: رس اصلاح‌شده + رس اصلاح‌نشده (۱:۱) مخلوط با نفت) در مقایسه با مالچ‌های ۱ (نسبت ۵:۱، خاک شنی: بنتونیت اصلاح‌نشده مخلوط با نفت) و ۳ (نسبت ۵:۱:۰.۵، خاک شنی: رس اصلاح‌نشده: رس اصلاح‌شده مخلوط با نفت) ترکیبات هیدروکربن‌های آروماتیک چند حلقه‌ای بیشتری را در خود نگه داشته است. تجزیه و تحلیل نمونه‌های آب رواناب نیز نشان داد که میزان حفظ PAHs در مالچ ۲ به طور قابل توجهی بیشتر از مقادیر حفظ‌شده توسط مالچ‌های ۱ و ۳ است.

## Graphical abstract



## Introduction

Petroleum pollutants and mobile dunes are two of the world's challenging environmental problems, in petroleum-producing countries located in arid and semi-arid regions. Each of these problems alone may cause serious damages to the environment and the economy of the petroleum-producing countries in the arid regions. However, an invention to stabilize dunes using petroleum waste materials tackles both problems and can turn them into an opportunity to improve environmental and socio-economic conditions. Further, such a solution can improve the physical, chemical, and fertility properties of the affected soils. Wind erosion influences about one-sixth of the land area worldwide (about 549 million ha) (Subramaniam and Chinappa, 2002), of which about 296 million ha are mainly located in arid and semiarid regions subjected to severe wind erosion (Lal, 2003). Iran is located in an arid and semiarid region and is subjected to severe wind and water erosion. Dust storms and mobile sand dunes are two urgent problems within the arid regions of Iran adversely impacting the cities, villages, roads, communication lines, facilities, and structures every year (Ekhtesasi and Hazirei, 2016). According to numerous studies, the areas affected by wind erosion in Iran are more than 34 million ha, of which more than 9 million ha in 178 active centers are in critical areas (i.e. coastal regions, sand dunes, plains, agriculturally important regions), and more than 30% of this, is classified as crucial areas (i.e. highly susceptible areas for wind erosion and dust storms) (Abbasi et al., 2019). The following provinces of Iran have the highest areas of wind erosion and deposition: Sistan and Baluchestan with 5.6, South Khorasan with 4.76, Khuzestan with 1.84, Khorasan Razavi 1.25, Yazd 1.22, Kerman 1.2, Isfahan 1.092, Markazi 0.9, Semnan 0.54, Qom 0.47, Bushehr 0.46, Hormozgan 0.318, North Khorasan 0.184, Alborz 0.12, Tehran 0.105 Mha. Recent studies show that the extent of dunes in Iran is about 4.8 Mha. The extent of mulched areas is 256814 ha, which covers about 3% of the area of the wind erosion critical zones and 4.5% of the total area of dunes in Iran (Research Institute of Forests and Rangelands, 2018).

To counter these soil erosion rates, various protection methodologies are used to protect dunes around the world. The biological stabilization is one of the stabilization methods, however, biological mulches are very expensive and do not have significant stability (Majdi et al., 2006). Other mulches being used include sugarcane (Khalili Moghadam et al., 2015a), petroleum combined with biological fixators (Khalili Moghadam et al., 2015b), micro silica with clay, gypsum (Naghizade Asl et al., 2019), and petroleum (Akbarnia, 2009). The mulch compounds (clay, polymer, petroleum, and organic matter) can increase sand cohesion and inter-particle resistance in sand dunes (Khalili Moghadam et al., 2015a). The main base of the petroleum mulches may contain heavy petroleum hydrocarbons such as saturated naphthenic, polar aromatics, and asphaltic materials (Akbarnia, 2009). Akbarnia et al. (2005), reported that the use of petroleum mulch increases dune stabilization through improved vegetation. Li et al. (2014) demonstrated that petroleum mulch enhances plant growth because of the rise of pores within the soil. Nevertheless,

there are many objections to the application of petroleum mulches to combat desertification and dune stabilization. Some scientist have stated that petroleum mulch poses a significant risk to the environment including by killing the animals, penetrating to the soil layers and polluting underground water, posing significant risk to human health (Akbal, 2005).

Recently, the production of efficient and inexpensive adsorbents for the reclamation of polluted environments has received more attention. Much study has been conducted on the modification of soil organic pollutants using reactive adsorbents and the use of these adsorbents has been accepted as a modification technology (Peggy and Dimitri, 2011). Clay due to its high surface area (Hu and Luo, 2010), availability, low cost (Gil et al., 2011), being ecofriendly and non-toxic, and its efficiency in sorption of various organic and inorganic pollutants in soil and aqueous media (Nourmoradi et al., 2013) is a valuable material to absorb of petroleum pollutants. However, unmodified clay cannot adsorb hydrophobic organic compounds because of the negative charges and hydrophilic characteristics of its surface. Therefore to enhance sorption capability, clay is usually modified with organic compounds. Cationic surfactants are materials commonly used to convert the hydrophilic properties of clay into hydrophobic properties. The sorption capacity of organics by clay (e.g. bentonite) is noticeably enhanced if the surface chemical properties of clay was modified using a surfactant (Ruan et al., 2014). Increasing the porous structure of clay after modification by surfactants increases its adsorption capacity and decreases its bulk density (Du et al., 2017). The retention of the adsorbed molecules depends on the  $\square$ mmobiliza power of the interlayer cations. Compared to monovalent and divalent ions, multivalent cations because of their strong electrostatic field retain larger amounts of the organic compounds. For instance the organo-ammonium ions not only provide hydrophobic interlayer spaces but also control the properties of the adsorbed compounds. The long amine chain in hexadecyl tri methyl ammonium bromide (HDTMA) binds to the hydrocarbons, and by electrostatic and van der Waal forces, fixes and holds them. High pollutant removal efficiency and cost-effectiveness are two major advantages of organoclay to remove organic pollutants (Akbal, 2005). Intercalation of cationic surfactants into clay minerals not only changes the surface properties of the clay from hydrophilic to hydrophobic but also greatly increases the adsorption capacity of anions in the interlayer space of the clay, especially when surfactant load is higher than the cation exchange capacity CEC of the clay.

Organoclays have been extensively investigated for the  $\square$ mmobilization of hydrophobic contaminants (Xi et al., 2010). Modified bentonite with organic surfactants, form a colloidal adsorbent for organic pollutants like polycyclic aromatic hydrocarbons (PAHs). PAHs include numerous organic compounds with various structures and varied toxicity, that are environmentally persistent. PAHs containing up to 6 aromatic rings are often referred to as “small” PAHs, and with more than 6 aromatic rings are classifies as large PAHs. The lower the number of rings and molecular weight of PAHs, the greater their

solubility in water. Naphthalene, for example, is a PAHs compound and has the smallest molecular mass and the highest solubility in water. Low Molecular Weight (LMW) PAHs have high vapor pressure and tend to convert the vapor phase in air. In contrast, the polyaromatic hydrocarbon compounds that have a higher number of rings and molecular mass, lower solubility in water, and a greater tendency to adhere to soil particles (Masih et al., 2012).

This study aimed to develop a method for the removal of petroleum pollutants released into the environment using modified bentonite, and to evaluate the use of petroleum-impregnated modified bentonite as an environmentally friendly and resistant mulch, to stabilize mobile dunes exposed to wind erosion.

## Section snippets

### Characteristics of bentonite and HDTMA

Three types of bentonites that are produced for industrial use in the mines of Tehran, Khorasan, and Zanjan provinces, were bought, and preliminary tests were performed on them to determine their properties. The types of anions and cations in the bentonite saturated extract (Sparks, 1996), the cation exchange capacity (CEC, Bower et al., 1952), and the amount of volume increase due to water adsorption, were measured for the studied bentonites. To determine the change in volume of bentonite due

### Chemical properties of bentonite

Among the studied bentonites, Tehran bentonite had the highest CEC which was equal to 70.76 cmol<sup>c</sup>/kg. Also the highest volume increase due to water absorption (about 5 times the original volume) was obtained for Tehran bentonite. Thus it was selected as a suitable bentonite for the purposes of this study. The saturation paste extract of Tehran bentonite was dominated by sodium cations ( $\text{Na}^+ = 146.7 \text{ cmol}^c \text{ L}^{-1}$ ) with lesser amounts of calcium ( $\text{Ca}^{2+} = 74.5 \text{ cmol}^c \text{ L}^{-1}$ ) and magnesium ( $\text{Mg}^{2+} = 28 \text{ cmol}^c \text{ L}$

## Conclusion

The objectives of this study were to find a solution to prevent the uncontrolled release of petroleum to the environment on one hand and to find a stable composition for fixing the dunes as a significant danger for environment and economy on the other. Our results showed that modified bentonite is capable of adsorbing petroleum several times its mass. The water repellency, hydraulic conductivity and water penetration of PIMB was corrected by dilution with unmodified sandy soil. The mulches

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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