

*M.A. Kalantaryan, A.K. Harutyunyan*  
**SURFACE-MODIFIED PUMICE FOR  
EFFICIENT REMOVAL OF OILY POLLUTANTS**

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## **SURFACE-MODIFIED PUMICE FOR EFFICIENT REMOVAL OF OILY POLLUTANTS**

**Marine A. Kalantaryan**

National University of Architecture and  
Construction of Armenia  
105, Teryan St. 0009, Yerevan  
e-mail: [kalantaryanm@mail.ru](mailto:kalantaryanm@mail.ru)  
ORCID iD: 0000-0001-9228-1978  
Republic of Armenia

**Arevik K. Harutyunyan**

Institute of Water Problems and Hydro-Engineering  
Named After I.V. Yeghiazarov  
125/3 Armenakyan St., 0011, Yerevan  
e-mail: [arevikkamoyevna@gmail.com](mailto:arevikkamoyevna@gmail.com)  
ORCID iD: 0009-0006-1554-5267  
Republic of Armenia

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### **Abstract**

Wastewater treatment has become a growing environmental challenge due to rapid urbanization and industrial development. Conventional physical, chemical, and biological treatment methods often suffer from high operational costs and generate secondary pollutants. Among alternative approaches, adsorption using natural materials has emerged as an effective and environmentally friendly solution owing to its high efficiency, low cost, and minimal secondary contamination.

Car washing stations generate large volumes of oily wastewater containing petroleum hydrocarbons, detergents, suspended solids, surfactants, and trace heavy metals. If discharged without proper treatment, these effluents can pose serious risks to aquatic ecosystems and soil quality, potentially exceeding permissible discharge standards.

In this study, pumice obtained from the Irind mine was investigated as a natural adsorbent for treating car wash wastewater. To enhance its performance, the pumice surface was modified with polysiloxane, a widely studied biomaterial known for its chemical stability. The modified pumice exhibited a 40% increase in adsorption efficiency compared to the unmodified material, demonstrating its potential as an effective and low-cost adsorbent for treating oily wastewater.

**Keywords:** basins, car washing station; pumice; surface modification; adsorption; wastewater treatment.

### **Introduction**

The Car wash facilities are among the major sources of dispersed oily wastewater, and the contamination of water resources by petroleum hydrocarbons has become a global environmental

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concern requiring urgent attention. During vehicle washing operations, motor oil, petrol, grease, lubricants, and detergent residues are released into wastewater streams [1]. If discharged without proper treatment, these contaminants can infiltrate soils, damage aquatic ecosystems, reduce oxygen transfer, form oil films on surface waters, and impair the performance of municipal wastewater treatment plants (WWTPs).

Car wash wastewater is characterized by its complex and highly variable composition, which depends on factors such as vehicle condition, washing techniques, detergents used, operational frequency, and the quantity of debris removed [2]. Rapid urbanization has significantly increased the volume of wastewater generated, prompting regulatory authorities to impose stricter discharge limits on sewage. Consequently, there is a growing interest in developing economical and environmentally friendly treatment methods for car wash effluents [3].

Car wash wastewater typically contains detergents, phosphates, oils, surfactants, suspended solids, and heavy metals [4]. Surfactants, which are widely used in cleaning agents, promote foam formation and contribute to eutrophication in receiving water bodies, leading to increased pH, oxygen depletion, and deterioration of aquatic ecosystems [5]. The presence of hydrocarbons, organic matter, and heavy metals further intensifies environmental and public health risks [6].

Conventional treatment of car wash wastewater often involves multistage processes. Primary treatments, such as sedimentation and oil–water separation, are effective for removing large particles and free-floating oils [7]. Secondary treatment methods, including coagulation–flocculation and advanced oxidation processes (AOPs), are used to reduce the organic load and turbidity. For example, coagulants such as ferric chloride and aluminum sulfate destabilize colloidal particles, facilitating their removal; however, these processes require precise chemical dosing and generate secondary sludge and by-products [8]. Ozonation, an advanced oxidation technique, is effective for degrading organic contaminants; however, it is associated with high energy consumption and operational costs [9].

Adsorption is a widely applied and efficient method for treating oily wastewater because of its simplicity, low operational cost, and high removal efficiency. The physical interactions, such as van der Waals forces, hydrophobic interactions, hydrogen bonding, polarity effects, steric interactions, dipole-induced dipole interactions, and  $\pi$ – $\pi$  interactions [10,11]. In this process, sorbate molecules accumulate on the external surface and within the pores of the adsorbent without penetrating its internal structure [12].

Oil adsorption generally proceeds through three main stages: dispersion of oil molecules onto the adsorbent surface, entrapment of oil within the porous framework via capillary action, and agglomeration of oil droplets within the rough and porous structure of the material [13]. Compared with conventional treatment methods, adsorption offers advantages such as low capital investment, operational simplicity, and flexibility. Although activated carbon is widely used as an effective adsorbent, its high cost and regeneration requirements limit its large-scale applications [14]. Therefore, alternative low-cost and efficient natural materials such as pumice are being increasingly explored.

In this study, pumice obtained from the Irind mine was modified with a polysiloxane solution to enhance its oil adsorption capacity for the treatment of car wash wastewater.

## **1. Materials and Methods**

### **1.1 Irind mine pumice**

The Republic of Armenia leads the world in terms of nonmetallic mineral diversity and abundance. The country has almost every type of mineral rock known globally. Light rocks (tuffs,

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perlite, pumice-stone, zeolite, scoria, etc.) are the most significant mountainous rocks formed by volcanic processes in Armenia.

Irind is located in the Talin region. It is 46 km from the regional center. The village has perlite and pumice resources of industrial importance. In the Republic of Armenia, pumices are divided into two types according to their physical and mechanical characteristics: Ani type and lithoid pumices [14, 15].

One type of Ani pumice was sourced from the Irind mine. This pumice primarily consists of non-crystalline (amorphous) glass particles, plagioclase, pyroxene, mineral crystals, and fragments of ancient lava. Its porosity ranges from 35% to 44%, and it typically appears yellowish, occasionally exhibiting a yellow-brown or pink-yellow hue. The thermal insulating properties of pumice are notably high. It has a bulk density of 0.3–0.6 g/cm<sup>3</sup> [16].

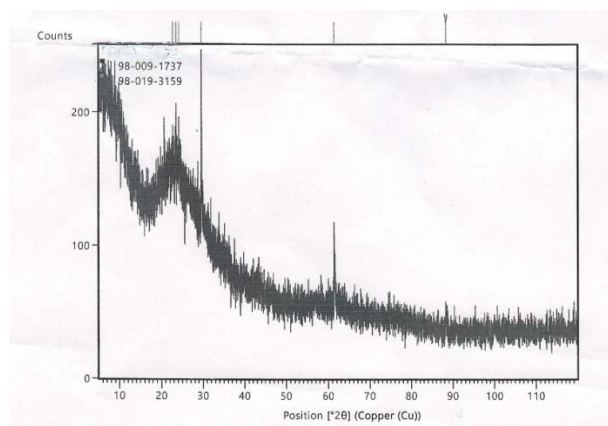
Studies have shown that the pumice is composed of aluminosilicates in which the amount of alkaline oxides is: SiO<sub>2</sub> -61.54 %, MgO - 1.13%, TiO<sub>2</sub> - 1.00%, Fe<sub>2</sub>O<sub>3</sub> - 3.99%, K<sub>2</sub>O +Na<sub>2</sub>O - 8.18 %, Al<sub>2</sub>O<sub>3</sub> - 16.58%, and CaO is 3.78 %.

**Table 1**

**Chemical composition of Irind mine pumice (wt. %)**

Oxide	Content (wt%)
SiO <sub>2</sub>	61.54
MgO	1.13
TiO <sub>2</sub>	1.00
Fe <sub>2</sub> O <sub>3</sub>	3.99
K <sub>2</sub> O +Na <sub>2</sub> O	8.18
Al <sub>2</sub> O <sub>3</sub>	16.58
CaO	3.78

The examination of the pumice by X-ray diffractometry has shown that it is a volcanic rock and is composed of cristobalite and coesite.



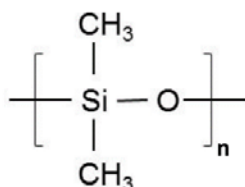
**Fig.1 X-ray Diffraction (XRD) analysis of pumice**

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Coesite and cristobalite are high-pressure polymorphs of silica, silicon dioxide (SiO<sub>2</sub>). They have the same composition but possess a different crystal structure [14].

### 1.2. Polysiloxane

Polysiloxanes are among the most extensively studied and utilized biomaterials owing to their inherent stability and biocompatibility. Their hydrophobicity, low surface tension, and heat stability render polysiloxanes ideal for manufacturing catheters and other medical devices [17,18]. In the laboratories of the chemical industry, polysiloxane is used as a mold release agent, lubricant, plasticizer, emulsifier, or defoaming agent. Many of these applications are made possible by the very low surface tension of polysiloxanes [19,20]. The chemical structure of polysiloxane is presented in Fig.2.



**Fig.2 Chemical structure of polysiloxane**

### 1.3. Wastewater

Car wash wastewater typically contains a complex mixture of physical, chemical, and biological pollutants. The most frequently reported contaminants include diesel and gasoline fractions, motor oils, lubricants, greases, and polycyclic aromatic hydrocarbons (PAHs). These compounds are predominantly hydrophobic and tend to form stable films or emulsions in water, making their removal particularly challenging using conventional treatment methods.

### 1.4. Surface modification

Before use and modification, pumice was washed several times with distilled water to remove any impurities and dried at a temperature of 40±10 °C. For chemical treatment using an acid solution, pumice was immersed and stirred in HCl 1 M for 3 h and washed using distilled water, then dried at 1300C for 3 h.

The optimum concentration of the modifier was 15% of the mass of the pumice; the ratio of the water to the solvent was 1:25. The emulsion of polysiloxane was added, thoroughly mixed, and dried at T = 60 °C for 8 hours until a complete hydrophobic effect occurs.

### Conflict Setting

The rapid growth of car washing stations has led to increased discharge of oily wastewater, posing serious environmental risks when inadequately treated. While effective, conventional treatment methods are often too costly and complex for small-scale facilities. This creates a conflict between environmental protection requirements and economic feasibility, highlighting the need for low-cost and efficient solutions such as surface-modified natural adsorbents.

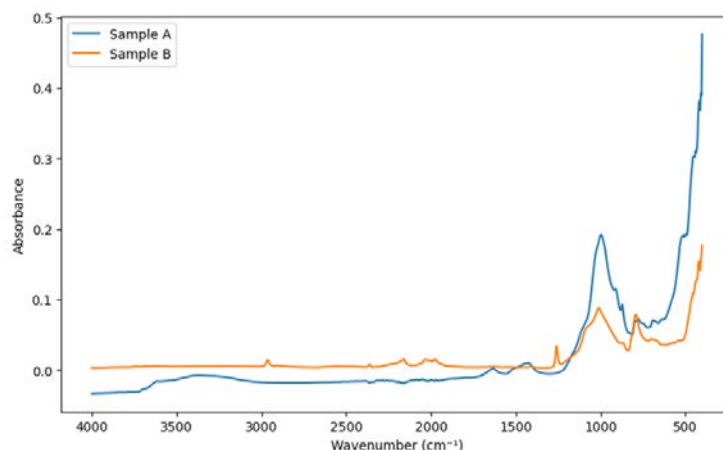
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## Research Results

### 2. Results and discussion

#### 2.1. FTIR investigation of polysiloxane modified pumice

Fig.3 shows the Fourier transform infrared (FTIR) spectrum of pumice before and after modification with polysiloxane.



**Fig.3 FTIR analysis of pumice**

**Sample A is the spectrum before modification**

**Sample B is the spectrum after modification**

The FTIR spectrum of the pumice sample reveals characteristic absorption bands confirming surface modification with polysiloxane. The absorption peak observed at approximately  $1260\text{ cm}^{-1}$  is attributed to the Si-CH<sub>3</sub> bending vibration, indicating the presence of methyl (C-H) groups. The strong absorption band in the region of  $\sim 1100\text{ cm}^{-1}$  corresponds to Si-O-Si stretching vibrations, which are characteristic of siloxane linkages. In addition, stretching vibrations detected at around  $\sim 2960\text{ cm}^{-1}$  are assigned to C-H stretching modes of methyl groups. The presence of these characteristic bands confirms that the surface of the pumice has been successfully modified with organic polysiloxane compounds, in agreement with previous studies [21].



**Fig 4. Standard laboratory cylindrical flask for filtration**

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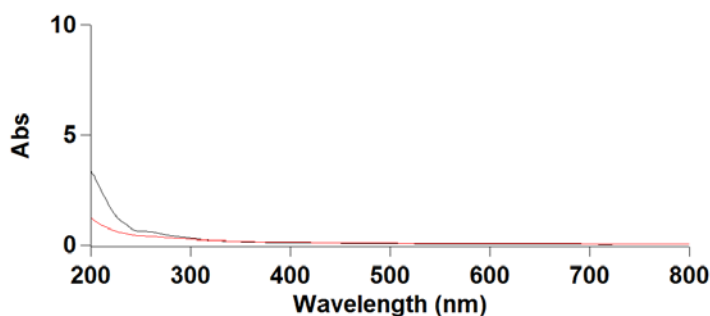
The study for water purification was carried out in standard laboratory cylindrical flasks with volumes of 150 ml. Based on the existing dimensions of these mini-filters (diameter and loading height), the speed of free-flow filtration was regulated using a valve located at the bottom. The average results of filtration speeds (1.5–3.0 mm/s) for the retention of petroleum products were observed.

## 2.2. Effects of contact time

To attain equilibrium throughout the batch process, the contact time and oil removal were regulated, as shown in Figure 4. Oil removal increased with longer contact times. Due to adsorbent surface modification, adsorption occurred on the surface between the first (20–30) and last (40–60) minutes of the experiment.

## 2.3. Concentration determination

Oil concentrations before and after adsorption were measured using a UV-Vis Spectrophotometer (Cary-60). The wavelength of 250.0 nm corresponds to the maximum absorbance of the oil on the pumice. After modification by polysiloxane, the absorbance increased by 40% compared with unmodified pumice (Fig. 5).



**Fig 5. UV-Vis spectrophotometric analysis**

## Conclusion

This study demonstrated the potential of pumice obtained from the Irind mine as a low-cost and effective adsorbent for the treatment of oily wastewater generated by car washing stations. XRD analysis confirmed the predominantly amorphous aluminosilicate structure of the pumice, which is favorable for adsorption processes. FTIR spectroscopy verified the successful surface modification of pumice with polysiloxane through the appearance of characteristic Si–CH<sub>3</sub>, Si–O–Si, and C–H functional groups, indicating the introduction of hydrophobic organic moieties.

Surface modification enhanced the adsorption performance of the pumice. The polysiloxane-modified pumice exhibited approximately **40% higher oil adsorption efficiency** compared with the unmodified material, which can be attributed to increased hydrophobicity and improved affinity toward nonpolar organic contaminants present in car wash wastewater. The adsorption mechanism is primarily governed by hydrophobic interactions between the modified pumice surface and petroleum-based pollutants.

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The results highlight that polysiloxane-modified pumice is a promising, environmentally friendly, and economical adsorbent for oily wastewater treatment. Its natural abundance, simple modification process, and improved adsorption efficiency make it suitable for practical applications in car wash wastewater treatment systems.

Future studies should focus on regeneration, reuse potential, and performance evaluation under continuous-flow conditions.

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**Մ.Ա. Քալանթարյան<sup>1</sup>, Ա.Կ. Հարությունյան<sup>2</sup>**

<sup>1</sup>Ճարտարապետության և շինարարության Հայաստանի ազգային համալսարան

<sup>2</sup>Ակադեմիկոս Ի.Վ. Եղիազարովի անվան ջրային հիմնահարցերի և հիդրոտեխնիկայի ինստիտուտ

Կեղտաջրերի մաքրումը դարձել է բնապահպանական խնդիր՝ պայմանավորված քաղաքաշինության և արդյունաբերական զարգացման հետ: Ֆիզիկական, քիմիական և կենսաբանական մաքրման մեթոդները հաճախ բնութագրվում են շահագործման բարձր ծախսերով և երկրորդային աղտոտիչների առաջացմամբ: Այլընտրանքային մոտեցումների շարքում բնական նյութերով ադսորբցիոն գործընթացը դիտարկվում է որպես արդյունավետ և շրջակա միջավայրի համար անվտանգ լուծում՝ շնորհիվ բարձր արդյունավետության, ցածր արժեքի և երկրորդային աղտոտման նվազագույն մակարդակի:

Ավտոլվացման կայանները արտադրում են մեծ քանակությամբ յուղային կեղտաջրեր, որոնք պարունակում են նավթային ածխաջրածիններ, լվացող միջոցներ, կախյալ մասնիկներ, մակերևութաակտիվ նյութեր և աննշան քանակությամբ ծանր մետաղներ: Առանց համապատասխան մաքրման շրջակա միջավայր արտանետվելու դեպքում նման կեղտաջրերը կարող են լուրջ վտանգ ներկայացնել ջրային էկոհամակարգերի և հողի որակի համար՝ հաճախ գերազանցելով սահմանային թույլատրելի կոնցենտրացիաները:

Սույն աշխատանքում Իրինդի հանքավայրի պեմզան ուսումնասիրվել է որպես բնական ադսորբենտ ավտոլվացման կեղտաջրերի մաքրման համար: Դրա արդյունավետությունը բարձրացնելու նպատակով պեմզայի մակերեսը մոդիֆիկացվել է պոլիսիլոքսանով՝ քիմիական կայունությամբ հայտնի և լայնորեն ուսումնասիրված կենսանյութով: Մոդիֆիկացված պեմզան ցուցաբերել է ադսորբցիոն ունեցվածքանմուտ 40 % աճ՝ համեմատած չմոդիֆիկացված նյութի հետ, ինչը հաստատում է դրա կիրառելիությունը որպես արդյունավետ և ցածրարժեք ադսորբենտ յուղային կեղտաջրերի մաքրման համար:

**Բանալի բառեր.** ավտոլվացման կայան; պեմզա; մակերեսի մոդիֆիկացում; ադսորբցիա; կեղտաջրերի մաքրում:

## **МОДИФИКАЦИЯ ПОВЕРХНОСТИ ПЕМЗЫ И ЕЁ ПРИМЕНЕНИЕ ДЛЯ УДАЛЕНИЯ СМАЗОЧНЫХ МАСЕЛ ИЗ ВОДНЫХ СРЕД**

**М. А. Калантарян<sup>1</sup>, А.К. Арутюнян<sup>2</sup>**

<sup>1</sup>Национальный университет архитектуры и строительства Армении

<sup>2</sup>Институт водных проблем и гидротехники им. акад. И.В.Егизарова

Очистка сточных вод стала одной из нарастающих экологических проблем, обусловленных быстрым процессом урбанизации и развитием промышленности. Физические, химические и биологические методы очистки часто характеризуются высокими эксплуатационными затратами и образованием вторичных загрязняющих веществ. Среди альтернативных подходов адсорбция с использованием природных материалов

*M.A. Kalantaryan, A.K. Harutyunyan*  
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рассматривается как эффективное и экологически безопасное решение благодаря высокой эффективности, низкой стоимости и минимальному вторичному загрязнению.

Автомоечные станции образуют значительные количества маслосодержащих сточных вод, включающих нефтяные углеводороды, моющие средства, взвешенные частицы, поверхностно-активные вещества и малые количества тяжелых металлов. При сбросе без надлежащей очистки стоки могут представлять серьезную угрозу для водных экосистем и качества почв, зачастую превышая предельно-допустимые концентрации.

В настоящем исследовании пемза, добытая на месторождении Иринд, была изучена в качестве природного адсорбента для очистки сточных вод автомоек. Для повышения ее адсорбционных свойств поверхность пемзы была модифицирована полисилоксаном — широко исследуемым биоматериалом, известным своей химической стабильностью. Модифицированная пемза продемонстрировала увеличение адсорбционной эффективности на 40 % по сравнению с немодифицированным материалом, что подтверждает ее потенциал в качестве эффективного и низкзатратного адсорбента для очистки маслосодержащих сточных вод.

**Ключевые слова:** автомоечная станция; пемза; модификация поверхности; адсорбция; очистка сточных вод.

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