

INVESTIGATION OF TiO₂ AND ZnO NANOPARTICLES COATED ON RAW PUMICE FOR EFFICIENT REMOVAL OF ETHIDIUM BROMIDE FROM AQUEOUS SOLUTIONS

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ABSTRACT

Ethidium bromide is a strong mutagen and is also very toxic at acute exposures. It is classified as a potent mutagen. Therefore, the main aim of this research is to study the efficiency of raw and modified pumice in the adsorption of Ethidium bromide from synthetic solutions. Initially, the pumice used in the present study was kept in 0.1 N HCl for 24 hours. Thereafter, it was washed repeatedly with distilled water and was oven dried at 105°C for 24 hours. Then, the dried samples were ground and were passed through 20-30 mesh sieves with effective size of 2-3 mm. The floating method was used to coat zinc and titanium dioxide nanoparticles onto the adsorbent. A spectrophotometer was used to determine the concentration of Ethidium bromide based on the absorption at the wavelength of 285 nm. The results showed that as contact time increases, the adsorption capacities of the three adsorbents also increase. The equilibrium time was determined to be 60 min for used adsorbents. The equilibrium adsorption data tended to fit with the second pseudo order kinetic. Adsorption rate constants (K^2) for modified pumice with TiO₂ and ZnO were several times more in comparison with raw pumice. The results showed that by coating TiO₂ and ZnO onto raw pumice, the adsorption capacity and also adsorption rate were significantly increased. Moreover, pumice modified with ZnO showed a more adsorption capacity than pumice modified with TiO₂.

KEYWORDS:

Ethidium bromide, Natural pumice, Nanoparticles, Adsorption isotherms

INTRODUCTION

Ethidium bromide (EtBr; 3,8-diamino-6-phenyl-5-ethylphenanthridinium) is a chemical with

trade name of Homidium Bromide; Dromilac and chemical formula of C₂₁H₂₀N₃Br. Ethidium bromide is a nonvolatile, crystalline, dark solid and is soluble in water which fluoresces readily with a reddish brown color when it is exposed to ultraviolet light [1-3]. Ethidium bromide is widely used as a nonradioactive DNA stain to detect and visualize nucleic acid bands in electrophoresis method and perform other methods of nucleic acid separation [3-5]. Ethidium bromide is a potent mutagen and is also very toxic at acute exposures. It is classified as a potent mutagen [4, 6, 7]. Ethidium bromide can be absorbed through skin, so it is important to avoid direct contact with this chemical. It is an irritant to the skin, mouth, eyes, and upper respiratory tract [2, 6]. The U.S EPA does not currently regulate Ethidium bromide as a hazardous waste. Because of its highly mutagenic nature, however, authorities either prohibit Ethidium bromide discharges, or only allow it in very dilute concentrations in municipal wastewaters [3, 6, 8]. Residual of Ethidium bromide remains after use in the wastes and wastewater and enter life cycle due to the various application of the chemical. Therefore, some level of treatment is necessary before being discharged directly into the environment. Various methods such as chemical oxidation [6], adsorption [6], XAD resin [9], mono walled carbon nanotubes [2, 10], electrochemical processes [4], photo catalytic processes [5, 7, 11], etc. are used by researchers in the removal of Ethidium bromide. Adsorption has been developed as an effective approach for the removal of Ethidium bromide [6]. In literature, only few methods such as activated carbon and multi walled carbon nanotubes have been used for the removal of Ethidium bromide. Therefore, there is an urgent need to develop inexpensive and more effective techniques. Pumice is an effective, economical and easily available worldwide adsorbents that has been widely used for the removal of contaminants of water and wastewater [12-20]. Pumice is a porous (porosity above 85%) and light volcanic rock. Pumice's pores

are irregular in shape and generally not well connected to each other inside. Pumice contains a high percentage of silica in its composition (approximately 60% to 70% SiO₂) and typically has a Mohs hardness of 5 to 5.5 [14]. Taking into account these characteristics of pumice, the aim of the present study were to evaluate feasibility of raw and modified pumice in the removal of Ethidium bromide from synthetic solutions.

MATERIALS AND METHODS

Preparation and characterization of the adsorbents. Pumice used in the present study was obtained from Tikmedash region in eastern Azarbayejan province, Iran. The adsorbent was then placed in HCl 0.1 N for 24 hr in order to increase the porosity and removal of dirt. Thereafter, it was washed several times with double distilled water until the turbidity of washed water reduced to below 0.1 NTU. Then, the pumice samples were oven dried at 105 °C for 16 hr. Later the dried sample was crushed and sieved through the meshes 20-30 with effective size of 2-3 to obtain smaller particle sizes. After that, the pumice was modified with ZnO and TiO₂ nanoparticles. The floating method was used to coat ZnO and TiO₂ nanoparticles onto the adsorbent.

500 ml double distilled water was poured into a beaker and 1 g of ZnO and TiO₂ nanoparticles was added and the mixture was shaken at 300 rpm for 30 min. Then, 100 gr of the prepared pumice was added into the solution and agitated completely for 1 hr. Thereafter, the powder was oven dried at 100 C for 24 hours. Finally, in order to obtain modified pumice, the dried powder was placed into a furnace

to coat the ZnO and TiO₂ nanoparticles on it. The pumice nanoparticles and modified pumice nanoparticles were placed in a dry place to be used for the adsorption experiments. Structure, morphology and surface properties of nanostructured particles and the functional groups were studied.

Adsorption experiments. This experimental study was carried out in batch manner in a 100 ml Erlenmeyer flask placed on a shaker. Ethidium bromide powder was used through the tests to prepare desired concentrations of Ethidium bromide solution. Doubled distilled water was used for the preparation of stock solutions. Initially, 10 ml of the sample with a desired concentration was added into an Erlenmeyer flask and the pH of the solution was adjusted using NaOH and HCl. Then, a desired weight of the adsorbent was added into Erlenmeyer flask and placed immediately on a shaker. As the shaking time passed, the sample was filtered through 0.45 μm Millipore filters. Then, the concentration of Ethidium bromide was determined in the filtered samples.

The effect of system variables such as initial concentration of Ethidium bromide, adsorbent dose and contact time were investigated.

Analysis. Concentration of Ethidium bromide was measured spectrophotometrically at 285 nm according to the Standard Methods for Examination of Water and Wastewater [21]. The SEM test was performed for adsorbents morphology determination. All the chemicals and materials used in the study were purchased from Merk Company and the results were analyzed by use of Excel.

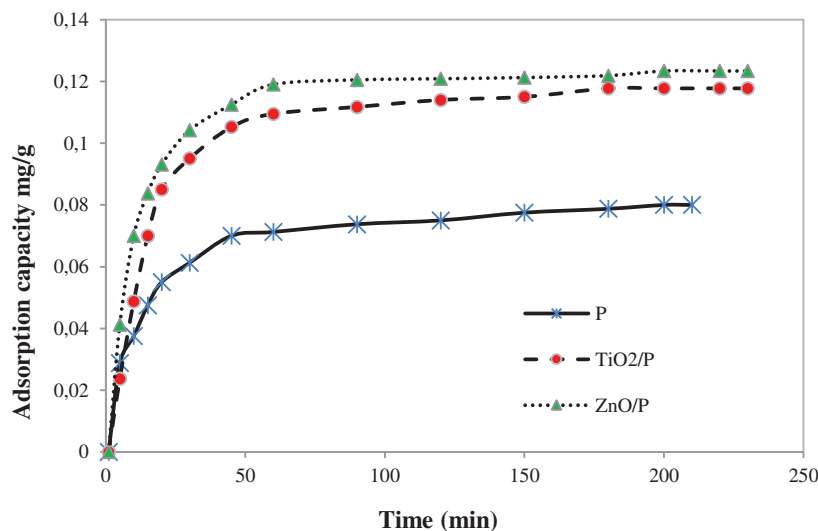


FIGURE 1
Effect of contact time (pH=2, initial Ethidium bromide=1 mg/l, adsorbent dose=4 g/l, agitation speed=150 rpm)

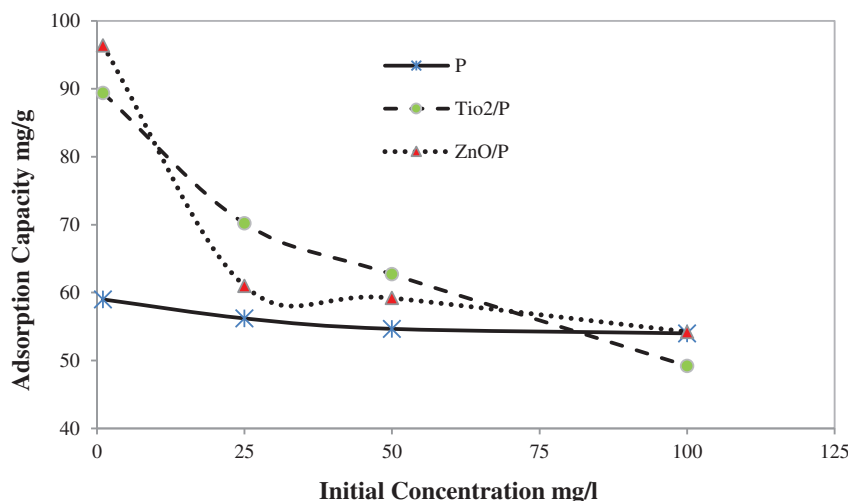


FIGURE 2
Effect of initial concentration (pH=2, contact time=60 min,
adsorbent dose=4 g/l, agitation speed=150 rpm)

RESULTS AND DISCUSSION

Effect of contact time. Effect of contact time on the removal efficiency is shown in Fig.1. As can be seen from the figure, the adsorption capacities of these three adsorbents increase with the increase in contact time. The increase was significant until 60 min of reaction and then remained almost constant for the remaining time which shows that, the adsorption reached the equilibrium for P, TiO₂/P and ZnO/P adsorbents. The adsorption capacity of the pumice significantly increases after modification of raw pumice with ZnO and TiO₂ nanoparticles. Adsorption capacity was 0.071 mg/g for P at 60 min which reached to 0.109 and 0.12 mg/g for TiO₂/P and ZnO/P after modification.

Effect of initial concentration. From Fig. 2 it is apparent that by increasing the initial concentration of Ethidium bromide, the removal efficiency increase for the three adsorbents. Inversely, adsorption capacities decrease. Moreover, difference among removal efficiencies for the three adsorbents is more significant at lower concentrations in comparison with higher ones. So, the percentage removal was 59, 89.4 and 96% for P, TiO₂/P and ZnO/P, respectively at concentration of 1 mg/l of Ethidium bromide.

Effect of adsorbent dose. The effects of adsorbent doses on the adsorption capacity of Ethidium bromide are demonstrated in Fig. 3. As can be seen from the figure, an inverse relationship exists between adsorption capacity and adsorbent dose at this rate of progress. At dosage of 1 g/l of P, TiO₂/P

and ZnO/P, the maximum adsorption capacities were determined to be 0.29, 0.47 and 0.52 mg/g, respectively which decreased to 0.067, 0.09 and 0.096 mg/g at dosage of 10 g/l. In the present work, it was found that the percentage removal increases with increase in amount of adsorbent dosage.

Adsorption kinetics. Adsorption kinetics herein describes the rate of adsorption of Ethidium bromide onto P, TiO₂/P and ZnO/P. The rate of adsorption controls the times required to reach adsorption equilibrium. Pseudo first and second order models were used to describe mass transfer rate of Ethidium bromide onto P, TiO₂/P and ZnO/P based on the adsorption data. The linear form of pseudo first order equation can be given as bellow:

$$\text{Pseudo-first order equation: } \log Ct = (K1/2.303) + \log C0 \text{ Eq. (1)}$$

Where Ct is the residual Ethidium bromide concentration at time t, C0 is the initial concentration of Ethidium bromide and K1 is the pseudo-first order rate constant (1/min). The linear form of pseudo second order equation can be given as:

Pseudo-second order equation:

$$\frac{1}{Ct} = K2t + \frac{1}{C0} \text{ Eq. (2)}$$

Where K² (mg/mg min) is the pseudo-second-order rate [2, 22].

Fig. 4a and Fig. 4b represent the experimental data and R² values. Fig. 4a and Fig. 4b also show pseudo first order equation and pseudo second order equations, respectively. By considering R² values, it is apparent that these three adsorbents obey the pseudo second order equation.

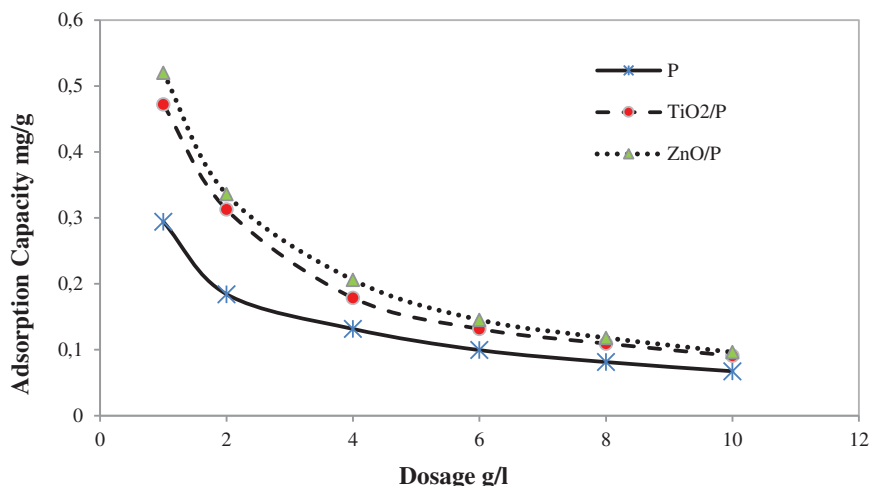


FIGURE 3

Effect of adsorbent dose (pH=2, initial Ethidium bromide=1 mg/l, contact time=60 min, agitation speed=150 rpm)

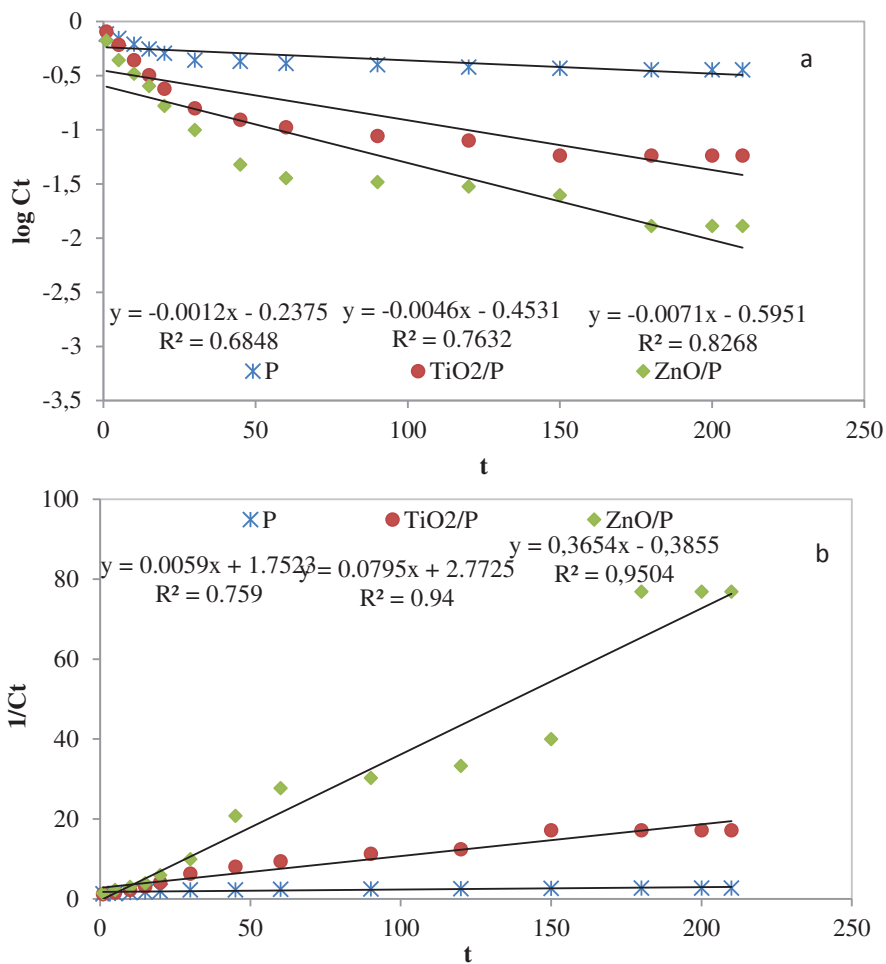


FIGURE 4

Ethidium bromide adsorption models onto raw pumice, pumice modified with TiO₂ and ZnO.
 a) Pseudo first order equation, b) Pseudo second order equation

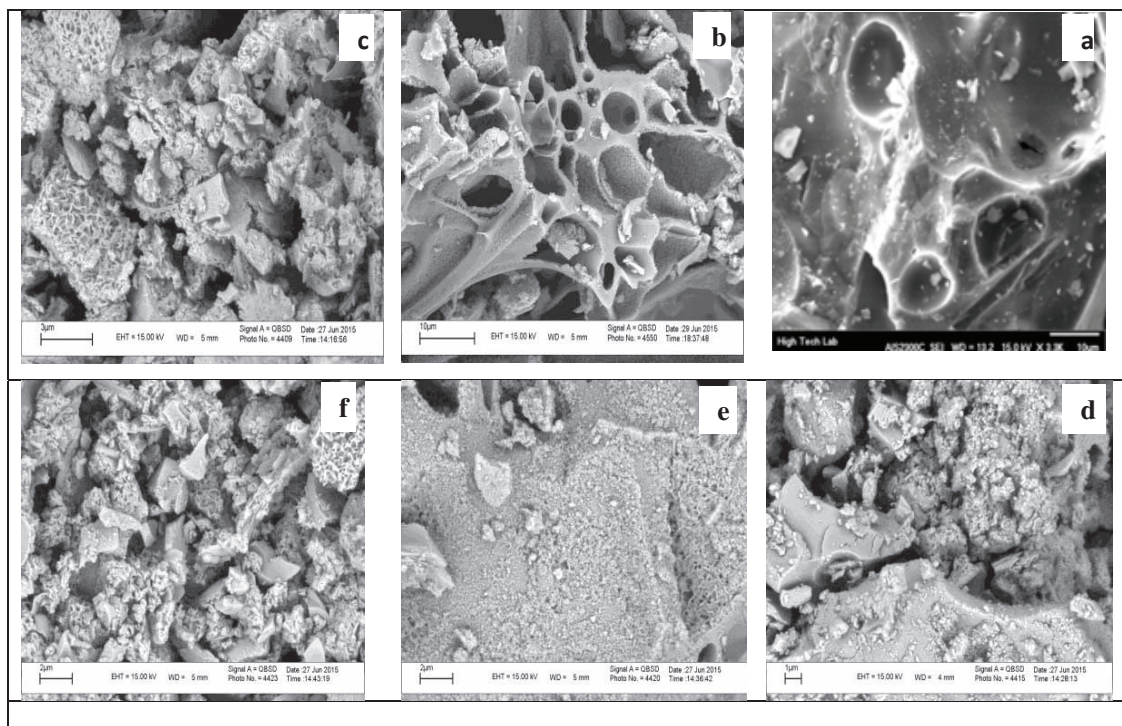


FIGURE 5

a) Raw pumice before adsorption, b) Raw pumice after adsorption, c) TiO₂/P before adsorption, d) TiO₂/P after adsorption, e) ZnO/P before adsorption, and f) ZnO/P after adsorption

Scanning electron microscopy (SEM) images of the adsorbents. Fig. 5 a, b, c, d, e and f show SEM images of raw pumice before adsorption, raw pumice after adsorption, TiO₂/P before adsorption, TiO₂/P after adsorption, ZnO/P before adsorption and ZnO/P after adsorption, respectively.

As the SEM images demonstrate, the high level of nanopore and micropore spaces are available on raw pumice that could be excellent for pollutant uptake (1) but by modification of raw pumice with nanoparticles significantly changes the morphological heterogeneity of the surface and creates more rough surface and non-uniform shape. Moreover, modification results in an increase in the number of surface pores. Fig. 5 b, d, f show images of raw pumice, pumice modified with nanoparticles after adsorption process. This increase in the number of the molecules on the surface indicates the progress of adsorption of Ethidium bromide onto the adsorbents.

Fig.1 displays effect of contact time on the adsorption of Ethidium bromide. As can be seen in the figure, the adsorption capacities have significantly increased after modification of the adsorbents by ZnO and TiO₂ nanoparticles. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the nanoparticles. Moreover, as SEM images demonstrate, after modification of the adsorbents with nanoparticles, more rough surface, and non-

uniform shape becomes available which totally increase the surface area for adsorption. From these figures it can be shown that the removal of Ethidium bromide increases with increasing the contact time until 60 min for these three adsorbents. At the beginning of the process, the adsorption rate was rapid and later it decreased gradually until 60 min. The higher sorption rate at initial period can be attributed to the increase of number of vacant binding sites available on the adsorbent until all these sites on the sorbent are saturated with no further increase in uptake. This observation is similar to that reported by Moradi et al and Ghaedi et al. [2, 23, 24]. The kinetic studies indicated that the process obeys the pseudo second order model. This agrees with the finding of pirsahab et al. [25]. This can be seen in R² values which were 0.759, 0.94 and 0.95 for P, TiO₂/P, ZnO/P, respectively. At the beginning of the process, the adsorption rate was rapid and reached the equilibrium gradually with the proceeding of reaction. According to adsorption rate constant (K²) in the present study, it is clear that coating nanoparticles onto raw pumice significantly increase the rate of adsorption. The values of K² were found to be 0.59×10⁻², 7.9×10⁻² and 36.54×10⁻² mg/g min for P, TiO₂/P, ZnO/P, respectively, signifying that adsorption rate of Ethidium bromide by TiO₂/P is 10 times as that of P and also the rate for ZnO/P is 5 times than that of TiO₂/P.

The results also clearly indicated that the

removal efficiency of Ethidium bromide increases by 30% after modification of adsorbents. By increasing the concentration of Ethidium bromide, the percentage removal decreases, indicating that at high-level concentrations of adsorbate molecules, the available sites of adsorption become fewer. This agrees with the finding of Moradi et al. [2], Pirsaeheb et al. [25]. It is readily understood that by increasing the adsorbent dose, the adsorption capacity decreases. As the adsorbent dose increases, more available adsorption surface area is provided. Considering the fact that the number of adsorbate molecules is the same, it therefore results in a decrease in the adsorption capacity, but totally the removal efficiency increases [26]. These results agree with the findings of other studies [26, 27]. The number of molecular collisions of the pollutant with the adsorbents increases as the agitation rate increases, so an increase in agitation accelerates the adsorption rate [26]

CONCLUSION

In general, the results of the present study showed that by coating TiO₂ and ZnO onto raw pumice, the adsorption capacity and also adsorption rate were significantly increased. Moreover, pumice modified with ZnO showed a more adsorption capacity than pumice modified with TiO₂.

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REFERENCES

- [1] Green, F.J. (1990). The Sigma-Aldrich Handbook of Stains, Dyes and Indicators, Aldrich Chemical Company. Inc, Milwaukee, Wisconsin. 318.
- [2] Moradi, O., Fakhri, A., Adami, S., Adami, S. (2012). Isotherm, thermodynamic, kinetics and adsorption mechanism studies of Ethidium bromide by single-walled carbon nanotube and carboxylate group functionalized single-walled carbon nanotube. *Journal of colloid and interface science*.
- [3] Bountiff, L., Levantis, P., Oxford, J. (1996). Electrophoretic analysis of nucleic acids isolated from scrapie-infected hamster brain. *Journal of general virology*. 77(9), 2371-8.
- [4] Zhang, C., Liu, L., Wang, J., Rong, F., Fu, D. (2013). Electrochemical degradation of ethidium bromide using boron-doped diamond electrode. *Separation and Purification Technology*.
- [5] Carbajo, J., Adán, C., Rey, A., Martínez-Arias, A., Bahamonde, A. (2011). Optimization of H₂O₂ use during the photocatalytic degradation of ethidium bromide with TiO₂ and iron-doped TiO₂ catalysts. *Applied Catalysis B: Environmental*. 102(1), 85-93.
- [6] Lunn, G., Sansone, E.B. (1987). Ethidium bromide: destruction and decontamination of solutions. *Analytical biochemistry*. 162(2), 453-8.
- [7] Adán, C., Bahamonde, A., Martínez-Arias, A., Fernández-García, M., Pérez-Estrada, L., Malato, S. (2007). Solar light assisted photodegradation of ethidium bromide over titania-based catalysts. *Catalysis Today*. 129(1), 79-85.
- [8] EPA. Environmental Health & Safety. University of California at Irvine. (<http://www.ehs.uci.edu>).
- [9] de-Oliveira, M.W., Hilsdorf, A.W., de-Souza, A.F., Oliveira, A.F. (2009). Estudo da adsorção de brometo de etídeo em resina XAD-7. *Quim Nova*. 32(5), 1134-8.
- [10] Najafi, F., Norouzi, M., Zare, K., Fakhri, A. (2013). Removal of ethidium bromide by carbon nanotube in aqueous solution: isotherms, equilibrium mechanism studies, and its comparison with nanoscale of zero valent iron as adsorbent. *Journal of Nanostructure in Chemistry*. 3(1), 60.
- [11] Adán, C., Martínez-Arias, A., Fernández-García, M., Bahamonde, A. (2007). Photocatalytic degradation of ethidium bromide over titania in aqueous solutions. *Applied Catalysis B: Environmental*. 76(3), 395-402.
- [12] Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research*. 33(11), 2469-79.
- [13] Gupta, V. (2009). Application of low-cost adsorbents for dye removal—A review. *Journal of Environmental Management*. 90(8), 2313-2342.
- [14] Karimaian, K.A., Amrane, A., Kazemian, H., Panahi, R., Zarrabi, M. (2013). Retention of phosphorous ions on natural and engineered waste pumice: Characterization, equilibrium, competing ions, regeneration, kinetic, equilibrium and thermodynamic study. *Applied Surface Science*. 284, 419-431.
- [15] Karimaian, K., Amrane, A., Kazemian, H., Panahi, R., Zarrabi, M. (2013). Retention of phosphorous ions on natural and engineered waste pumice: Characterization, equilibrium, competing ions, regeneration, kinetic, equilibrium and thermodynamic study. *Applied*

- Surface Science. 284, 419–431
- [16] Akbal, F. (2005). Sorption of phenol and 4-chlorophenol onto pumice treated with cationic surfactant. *Journal of Environmental Management*. 74(3), 239-244.
- [17] Noori Sepehr, M., Sivasankar, V., Zarrabi, M., Senthil Kumar, M. (2013). Surface modification of pumice enhancing its fluoride adsorption capacity: an insight into kinetic and thermodynamic studies, *Chemical Engineering Journal*. 228, 192-204.
- [18] Moraci, N., Calabrò, P.S. (2010). Heavy metals removal and hydraulic performance in zero-valent iron/pumice permeable reactive barriers. *Journal of Environmental Management*. 91(11):2336-2341.
- [19] Ozturk, B., Yildirim, Y. (2008). Investigation of sorption capacity of pumice for SO₂ capture. *Process Safety and Environmental Protection*. 86(1), 31-36.
- [20] Kitis, M., Kaplan, S., Karakaya, E., Yigit, N., Civelekoglu, G. (2007). Adsorption of natural organic matter from waters by iron coated pumice. *Chemosphere*. 66(1), 130-138.
- [21] APHA., AWWA., WEF. (2005). *Standard Methods for the Examination of Water and Wastewater*. 20 ed. American Public Health Association, Washington, DC.
- [22] Khosravi, R., Fazlzadehdavil, M., Barikbin, B., Taghizadeh, A. A. (2014). Removal of hexavalent chromium from aqueous solution by granular and powdered Peganum Harmala. *Applied Surface Science*. 292, 670–677
- [23] Ghaedi, M., Ghaedi, A.M., Negintaji, E., Ansari, A., Mohammadi, F. (2014). Artificial neural network– Imperialist competitive algorithm based optimization for removal of sunset yellow using Zn(OH)₂ nanoparticles-activated carbon. *Journal of Industrial and Engineering Chemistry*. 20(6), 4332-4343.
- [24] Moradi, O., Norouzi, M., Fakhri, A., Naddafi, K. (2014). Interaction of removal Ethidium Bromide with Carbon Nanotube: Equilibrium and Isotherm Studies. *Journal of Environmental Health Sciences & Engineering*. 12(1), 17.
- [25] Pirsaeheb, M., Dargahi, A., Hazrati, S., Fazlzadehdavil, M. (2014). Removal of diazinon and 2,4-dichlorophenoxy-acetic acid (2,4-D) from aqueous solutions by granular-activated carbon. *Desalination and Water Treatment*. 52(22-24), 4350–4355.
- [26] Abdoallahzadeh, H., Alizadeh, B., Khosravi, R., Fazlzadeh, M. (2016). Efficiency of EDTA modified nanoclay in removal of humic acid from aquatic solutions. *Journal of Mazandaran University of Medical Sciences*. 26(139), 111-125.
- [27] Fakhri, A., (2014). Assessment of Ethidium bromide and Ethidium monoazide bromide removal from aqueous matrices by adsorption on cupric oxide nanoparticles. *Ecotoxicology and Environmental Safety*. 104, 386-92.

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