Dinitrobutylphenol Removal from aqueous Environments by Synthesized magnetic particles from walnut hard-shell ash

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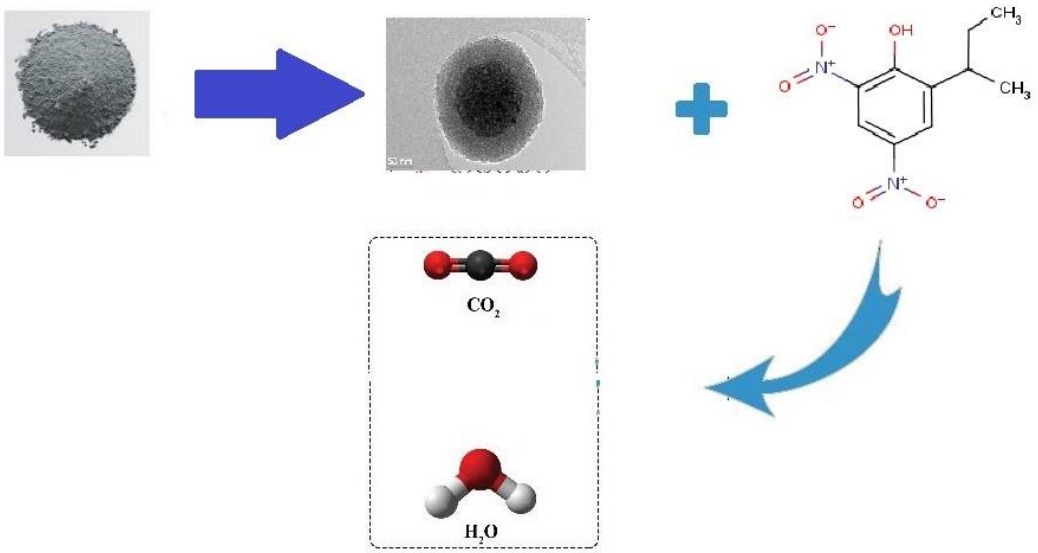
GRAPHICAL ABSTRACT



Abstract

Dinitrobutylphenol is a toxic and resistant pollutant that pollutes the environment by producing toxins and chemical wastewater. Present paper aims to study the efficiency of the magnetic particles

of walnut hard-shell ash as a cheap and bi-compatible adsorbent for the removable of DNBP from aqueous environments. This study was conducted at laboratory scale and studied the most important parameters including contact time, pH, adsorbent dose, concentration of the pollutant and temperature on the efficiency of the process. Walnut hard-shell ash was magnetized, and its properties were studied using SEM, FTIR, XRD, and BET techniques. The fitness of the data was studied using Langmuir and Freundlich isotherms. Results showed that at pH=7, temperature 25°C, 700 mg of adsorbent, within 50 min, the removal efficiency of DNBP with the initial concentration of 20 mg reached 93%. The isotherm studies showed that this process with fitness coefficient of 99% conforms to Langmuir equation and it has higher conformity to maximum adsorption of 142.88 mg/g. Magnetic particles of walnut hard-shell ashes as a natural bio-friendly and cheap adsorbent is able to efficiently remove DNBP as a toxic and persistent material from aqueous environments and industrial wastewaters.

Key words: Adsorption, DNBP, toxin, Isotherms, phenol, kinetic

INTRODUCTION

Phenolic pollution has arisen as an important problem in terms of its carcinogenicity and high toxicity as well as creating unpleasant taste and odor in water resources. The main sources of phenol and chlorophenols are refineries; petrochemical industries; industrial resins; plastics; rubber, aluminum,iron, steel, pulpand paper industries; pesticides; herbicides; fungicides; bactericides; including oils, softeners and electrical industries(Gholizadeh et al., 2013). The guideline proposed by WHO for phenol concentration in drinking water is <2 μg/L (Zeng et al 2009).

Complete removal or in some cases reduction of it to an acceptable concentration has become amajor challenge for environment protection (Shokoohi et al., 2019). DNBP is produced during the processes of making different combinations for various purposes. So it can enter surface waters and cause side effects such as toxicity and be carcinogenicity. Due to the large number of problems caused by these compounds, Environmental Protection Agency (EPA) has assigned strict

regulations for its maximum concentration in drinking water. This compound is resistant against microbial degradation and is hardly removed from wastewater by common methods of treatment (Wang et al., 2009). In order to remove phenol and phenol compounds from water, different advanced oxidation methods such as hydrogen peroxide, potassium permanganate, sulfur dioxide, ozone and biological methods have been used (Busca et al., 2008). Also, methods such as sequestration, settlement, filtration, adsorption, osmosis and ion exchange have been used for this purpose (Wang et al., 2010). The methods mentioned contain limitations such as sludge production, being time consuming and slow kinetics and high operation cost. Adsorption method is considered as an effective and quick method compared to other treatment methods. Although activated carbon is widely used as adsorbent for phenol and phenol compounds removal from water, it has the disadvantage of high-cost and complex regeneration. The development of potential low-cost adsorbents with high adsorption capacity is essential for phenol and phenol compounds removal. In The last few years, many materials such as, green macro alga, bagasse fly ash, and synthetic resin have been used in phenol removal from aqueous solution (Jing et al.,2013; ling et al., 2009).

Nowadays, natural materials such as agricultural wastes as cheap adsorbents have been noticed by the researchers in this field. Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seemed to be viable option for organic and inorganic treatment. Some of these wastes include the shell or core of materials such as almonds, pistachios, olive waste, peanut, and apricot (Ali et al., 2017). Degradation of solid agricultural waste leads to leakage of methane and latex and burning it by farmer's results in the production of carbon dioxide and other air pollutants. Thus, proper management of such a biomass including the production of adsorbent in addition to overcoming problems such as water and soil pollution, climate change, regional air pollution, and damage to environment. it has advantages such as reduction in the cost of treatment, local availability, etc. Therefore, converting such a biomass not only to energy but also to other materials is considered as an important challenge. During the past few decades, different agricultural wastes

have been used as low- cost adsorbents. (Mohan et al., 2011). Also, Wastes Produced from cereals like rice, corn, sugar beet and copra are included in this group (Bhatnagar et al., 2010). In this way, the use of these materials as adsorbent either without processing or by converting them into active carbon, results in a considerable increase in their economic value (EVs) and reduces disposal cost and more importantly it presents more appropriate solution for the production of active carbon (Salleh et al., 2011). therefore, adsorption using agricultural products have recently been introduced as a practical and economical method for the removal of different pollutants including phenol (Adegoke et al. 2015). There is an important limitation on the use of adsorbents that is, isolating them from the aqueous environment after treatment that less attention has been paid to it in the study mentioned. Filtration as a common method used for the isolation of the adsorbents is an erosion process that leads to blocking filters, losing the adsorbent and entering the sludge. One of the adsorbent isolation methods after treatment process is magnetizing these adsorbents that has been noticed by many researchers. Through magnetizing the adsorbents using magnetic compounds such as magnetite, we can readily isolate them from the environment using magnetic field after the process (Fayazi et al., 2015; Bastami et al., 2012).

Therefore, considering the points mentioned in this study, the synthesis of the magnetic adsorbent from the walnut hard-shell ash that is considered an agricultural waste and is abundant in most parts of the world, has been studied as a natural and cheap adsorbent in removing dinitro-butyl phenol.

MATERIALS AND METHODS

DNBP with chemical formula$C_{10}H_{12}N_2O_5$ and molecular weight 240.22 gr/mole was bought from Sigma-Aldrich Company. For synthesis of magnetic adsorbent from the walnut hard shell, Iron chloride ($FeCl_2$, $4H_2O$) (II), Iron chloride ($FeCl3$, $6H_2O$) (III) and ammonia were used. To adjust pH, sulfuric acid (H_2SO_4) and Sodium hydroxide (NaOH) produced by Mark Company were used and distilled water was used in preparing all solutions. To measure Dinitro-butyl phenol,

spectrophotometer (Dr 5000) was used (Shokrollahi et al., 2011). The adsorbent morphology under study was studied using SEM, (philips-XL30, Holland) EDS. The analysis of area (BET) Emmett-Teller Brunauer and pore size (BJH) Barrett-Halenda and volume analysis were carried out using Nitrogen Adsorbent Techniques (Micro-metrics/Gemini-2372). Functional groups on the adsorbent were analyzed using FTIR at wavelength of 400-4000 cm^{-1}. The crystal structure of magnetite available in the structure of the adsorbent was determined by XRD.adsorption isotherms defined by math models were studied and to determine the parameters of each model, the modeling and conformity of the experimental data must be fitted and finally after finding appropriate values for the parameters, the desired isotherm curve was drawn and its proximity to experimental data was studied. After the experiments, the balance of absorbent material per unit of the adsorbent (q_e) was obtained using Eq (1):

$$q_e = \frac{C_0 - C_e}{m_{ads}} \times V \qquad (1)$$

In this equation, C_0 is the initial concentration of DNBP in aquatic solution, C_e the balance concentration, V the volume of the solution in liter and mads the amount of adsorbent in gram (Zarei et al. 2015).***Synthesis of magnetic adsorbent of walnut hard shell***

First, the hard shell of walnut was ground and was washed with distilled water several times to clean the dust. Then, it was boiled in distilled water to remove the natural paint of walnut shell. In the next stage, for the purpose of removing settlements from cavities, acid-washing was carried out using normal nitric acid 0.001. After being washed and dried, the materials were put into the furnace at temperature of 700 $^{\circ}C$ for an hour (Divband et al., 2012). In continuation, for the purpose of magnetizing the related adsorbent using magnetite particles, first, 50 ml of distilled water solution was poured into the three- span Balloon and nitrification was carried out for 15 minutes, and in this way complete deoxygenating from environment was achieved. The balloon was put in the water bath of 85 $^{\circ}C$. Next, 0.21 gr of $FeCl_2, 4H_2O$ and 0.58 gr of $FeCl_3, 6H_2O$ (Molar ratio 2:1)

were added to the balloon and the solution was slowly stirred by a mechanical stirrer. 500 mg of the prepared adsorbent was added to the desired solution and it was stirred for 15 min. Then 5 cc of the 25% ammonia solution was added to the solution in drops using Burt until the pH reached above 9. It was stirred for another 30 min to complete the growth and magnetite particles. Finally, the magnetic adsorbent was isolated using magnet and it was washed with distilled water several times and was used for experiments (Bastami et al., 2012).

To evaluate the effect of the studied parameters on the efficiency of the process, the optimum pH was determined, then, at optimum pH, the removal efficiency of DNBP by adsorbent was determined in different values of other parameters. In the end, the magnetic adsorbent was isolated from environment using a magnet and the remaining concentration was measured.

RESULTS AND DISCUSSION

Effect of pH

One of the effective factors in pollutant adsorbent on adsorbent surface is the surface charge of the adsorbent that depends strongly on the pH of the solution. Therefore, studying the effect of the initial pH of the solution seems to be very necessary. To study the effect of solution's initial pH on the efficiency of removal process, the related processes were carried out and the results have been presented in Figure 1. Given the results, it is observed that at pH = 6, the removal efficiency is the highest, around 93%. On the other hand, at pH =7, the efficiency is around 90%, too, that is, only 3% lower compared to that of pH = 6. Thus, considering the point that the pH of DNBP solution is normally 6.5 and also given the considerations related to waste-water discharge in the environment or water resources, pH=7 was selected as optimal pH. As it was mentioned in previous section, the synthesized isoelectric adsorbent's pH is 6. Given that the structure of DNBP contains Nitro groups and Benzene ring. This material is expected to be absorbed better because of non-shared and ring electrons while it has adsorbent surface without charge or positive charge (Xiaohong et al., 2011).

At pH higher than isoelectric point, the adsorbent has negative surface charge, on the other hand, DNBP is packed with electrons because of the existence of Benzene Ring and Oxygen atoms. Hence, At high pH, the efficiency is lower due to the repulsion that is created. Similar results have been presented by Biglari on the removal of phenol from Aqueous Solutions using improve Zeolite (Biglari et al. 2019).

Figure 1. Effect of pH on the DNBP removal efficiency (DNBP= 20 mg/L and T= 25º C , reaction time = 50 min)***Identifying and determining adsorbent characteristics***

To study the characteristics of synthesized adsorbent in this paper, SEM, FTIR, XRD and BET methods were used. To study morphology of the synthesized adsorbent surface, scanning electron microscope (SEM) method was used whose related figure has been shown in Figure 2(a). Given the picture, it is observed that the synthesized adsorbent is porous and contains a large number of cavities. Also the results of EDS analysis revealed that the adsorbent contains carbon, oxygen, manganese, aluminum, silica, potassium and calcium: 90.22, 8.25, 0.16, 0.23, 0.16, 0.48 and 0.5 g/L, respectively. These elements are placed inside the cavities in oxide form, and given their low values, it could be concluded that the absorber has been properly prepared and cleansed.

X-ray diffraction method (XRD) is the most common method for identifying the crystal structure of the materials. Considering the existing classified information, we can easily identify the synthesized material and determine its phase. In this paper, XRD method was used to identify the magnetite in the structure of the adsorbent .The pattern obtained from XRD analysis of the related absorber, has been demonstrated in Figure 2(b). The peaks available in 2θs, 18, 30, 35, 43, 57, and 62 are related to magnetite particles in the structure of the adsorbent (Jiang et al., 2015).

FTIR analysis confirming the bonds between atoms and operational groups is available. The FTIR spectrum related to the synthesized adsorbent has been shown in Figure 2(c). The peak in 1422 cm^{-1} is related to CH_3 group and the identified peak in 1710 cm^{-1} belongs to operational group C=O. Also, the peaks in 1000 – 1300 cm^{-1} is related to tension bond of C – O, the wide peak in the range

of X-ray diffraction method (XRD) 3000- 3600 to $OH^{\cdot}$ group and the peak in 1586 cm^{-1} to operational group C = C. Also, peaks in the range of 500 - 650 cm^{-1} belong to Iron Oxide (Fayazi et al. 2015; Xiaohong et al. 2011; Zarei et al. 2015). Given the different operational groups in this adsorbent confirmed by FTIR spectrum, it could be concluded that this adsorbent will have adsorbent capability.

The chart related to isoelectric point determination of the magnetic adsorbent of walnut hard shell ash has been shown in Figure 2(d). Considering the point that the H^+ and OH^- are strongly absorb.

Thus, they can change the adsorbent surface charge. As it is seen in the Figure, pH_{pzc} is 6 for this adsorbent. In this way, if the pH of the solution is lower than pH_{pzc}, the charge of adsorbent will be positive and in the case that the solution pH is higher than that of pH_{pzc}, the charge of adsorbent surface will be negative. In general, adsorbent materials with opposite charge more.

The adsorbent surface area in square meters per gram by nitrogen adsorbent with purity of 99.999% at 77 $^{\circ}$K and using Brunauer Emmett Teller (BET) method was studied and the results showed that the amount of synthesized adsorbent surface was 291.45 m^2 /g. Also, the total volume of the cavities was 0.2407 cm^3/g and the mean number of cavities was 3.3 nm that the number obtained is significant compared to those of other studies (Hameed et al., 2008). The study of adsorbent surface with Langmuir Isotherm also showed that it was equal to 295.77 m^2/g. The study of the parameter of cavity volume distribution and the cavity surface using Barrett, Joyner, Halenda method (BJH) showed 0.1407 cm^3/g and 0.0459 m^2 /g for the volume and the surface of the cavities, respectively. Also, the study of the mica holes volume using t-plot showed that the volume of these holes was 0.074.

Figure 2. (a) SEM image of synthesized magnetic adsorbent, (b) XRD spectrum for magnetic adsorbent of walnut hard shell ash, (c) FTIR spectrum of magnetic adsorbent of walnut green shell, (d) point of zero charge (pH_{zpc}).

Studying the effects of main operational parameters in removing DNBP using synthesized adsorbent

To study the effect of effective parameters on DNBP removal efficiency from aqueous environments using synthesized adsorbent, parameters of contact time, pH, amount of adsorbent, pollutant concentration and temperature were studied and the results are presented as follows.

Effect of reaction time

To study the effect of contact time on the efficiency of DNBP removal by synthesized adsorbent, the process was carried out at different time periods. Results of study on the effect of contact time on DNBP solution with initial concentration of 20 mg/L using 500 mg/L of the synthesized adsorbent have been shown in Figure 3. As it is observed, the surface adsorbent rate of DNBP is high in the first thirty minutes of the reaction that is due to the high number of active sites available for the adsorbent of the pollutants but over time this steep reduces and after 40 minutes, the charges decrease and ultimately after 50 minutes, around 90% of the DNBP is removed.

In surface adsorbent process, over time with filling the adsorbent sites, efficiency gradually reduces until it reaches balance and the adsorbent is not able to absorb any more pollutants. Also, in reported studies, different time periods have been reported for various adsorbents. For example, in lead adsorbent with magnetized shell adsorbent that was carried out by Jiang and colleagues, the reaction time was reported 120 minutes (Jiang et al., 2015). In another study carried out to remove paint by magnetic adsorbent of Graphene and Chitosan by Sheshmani and Colleagues, 120 minutes was considered as the appropriate time for the process (Sheshmani et al., 2014). In comparing these processes, it is observed that the contact time for this process is lower compared to that of similar ones. The short time of surface adsorbent process can indicate that adsorbent occurs more in the surface of the adsorbent and the cavities are less involved. In the study conducted by Saeedi and Colleagues for the purpose of removing phenol by active phenol, almond and walnut shell carbon, a similar trend was reported concerning the changes in the process time (Saeidi et al., 2008).

Figure 3. Changes of DNBP removal efficiency over the reaction time (DNBP concentration= 20 mg/L and adsorbent dosage = 500 mg/L, T = 25 ^{o}C, pH = 7).

Effect of adsorbent dosage

With increasing the amount of adsorbent, the efficiency rises due to increase in adsorbent sites (Zarei et al., 2015) but overuse of adsorbent, wastes the process cost. To study the effect of the amount of adsorbent on removal efficiency, experiments at pH = 7 for 50 min with different values of adsorbent were conducted and the results have been presented in Figure 4. Given the Figure, it is observed that the removal efficiency of DNBP rises with increasing the amount of the adsorbent. As it is clear from the figure, with increasing the adsorbent from 100mg/L to 700 mg/L, the efficiency rises and after that no significant change is observed in efficiency. So, 700 mg/L of the adsorbent was selected optimal. In the study carried out by Godini and Colleagues on the effect of adsorbent dose of walnut green shell on phenol removal, the results showed that with increasing the adsorbent mass (weight) from 0.25 g to 5 g/L, the phenol removal efficiency rises (Hashemi et al., 2014).

However, there was a distinction between this study and Subramaniam study, as in their study, efficiency decreased by increasing the adsorbent concentration to a specified value (1.75g/l) . (Subramaniam et al., 2015).

Figure. 4. Effect of adsorbent dosage on the DNBP removal efficiency (T = 25^{o} C and pH = 7, Time = 40 min)

Effect of temperature

The surface adsorbent process, given the adsorbent mechanism and also mass transfer, could be affected by environment temperature (Subramaniam et al., 2015). To study the effect of temperature on removal efficiency, experiments were carried out at different temperatures whose results have been shown in Figure. (5). Considering the figure, it is observed that with increase in temperature

from 25ºC to 45ºC , the process efficiency has not changed significantly and after that with raising temperature to 70ºC , the process efficiency reduces to 91%. Thus, the temperature range, 25 – 40ºC, was selected as the optimal temperature. Increasing temperature in surface adsorbent process along with raising the amount of mass transfer, somewhat results in efficiency growth, but in higher temperatures in physical surface adsorbent process, the redu Relationship of phenol removal efficiency with increasing temperaturection in efficiency will be observed (Hill et al., 2014). The results obtained also confirm this finding. But the results of this study were in contrast to the research of Afsharnia and et al. The results of assessing the effect of temperature in the their study indicate that the absorption rate is elevated with increasing temperature because the increase in temperature enhances the number of collisions between particles and the surface of adsorbent.

Figure 5. Effect of temperature on the removal efficiency of DNBP (adsorbent dosage = 700 mg and pH = 7, reaction time = 40 min)

Effect of DNBP initial concentration

Results of study on DNBP initial concentration on the efficiency of surface adsorbent removal process by the ash of walnut hard shell have been shown in figure. Given the figure, it is observed that with increasing the initial concentration of DNBP from 20 mg to 150 mg, the removal process efficiency reduced from 99% to 63%. Given that the amount of the adsorbent is fixed, 700 mg, and the process has been studied for 40 min. At lower amounts of DNBP, more adsorbent positions are provided for pollutant molecules and as a result, removal efficiency will go up. With increasing the initial concentration, a competition is created between pollutant molecules for surface adsorbent. Thus, at a specific time at low concentrations, efficiency will increase (Zarei et al., 2015). In the study conducted by Hashemi and colleagues on the use of agricultural wastes in removing phenol from aqueous environments, it was revealed that with increasing the initial concentration of phenol, the adsorbent capacity of the adsorbent rises, whereas phenol adsorbent efficiency shows an inverse trend on the same day. The adsorbent results indicated that the removal efficiency was high at initial

concentrations and with increasing phenol initial concentration, removal efficiency reduces since the number of active adsorbent positions (places) on the surface of adsorbent for phenol reduces and this is due to filling adsorbent capacity and lack of efficiency at higher concentrations (Hashemi et al., 2014).

Figure 6. Effect DNBP initial concentration on the removal efficiency (adsorbent dosage = 700 mg, reaction time = 50 min, T = 25 ^{o}C, pH = 7)

Determining DNBP adsorbent isotherms

To study the Isotherm of DNBP surface adsorbent process on the magnetic adsorbent of walnut hard shell ash, experimental data were compared with the Isotherms of Langmuir and Freundlich, common Isotherms used in studies. Then, the experimental data were fitted with desired Isotherms in linear method.

Langmuir isotherm

Langmuir Isotherm is the most common and widely used Isotherm to study the surface adsorbent process. This Isotherm is a single-layer of analyte on adsorbent according to surface adsorbent process. Langmuir equation is stated in linear form according to Eq. (2) (Hameed et al., 2008).

$$\frac{C_e}{q_e} = C_e\left(\frac{a_L}{K_l}\right) + \frac{1}{K_L} \qquad (2)$$

In this equation, C_e is the balance concentration of DNBP, q_e the amount of pollutant absorbed on the surface, $a_L$and K_L the constants in Langmuir equation. The experimental data were compared with this Isotherm in linear method and the results have been presented in Figure 7(a). Given the figure, it is observed that the experimental data with fitness coefficient of 99% follow the Langmuir equation. Also, K_L =45.24 and a_L=0.316 were obtained for this process. To compute the highest adsorbent capacity (q_{max}), Eq (3) is used according to which the highest adsorbent capacity was achieved 142.88 mg/g.

$$q_{max} = \frac{K_l}{a_L} \quad (3)$$

Freundlich isotherm

Freundlich Isotherm is another isotherm that is widely used in the study of surface adsorbent. This isotherm explains surface adsorbent on heterogeneous surfaces and states that the pollutant is absorbed in the form of multi-layers on the adsorbent. Freundlich equation in linear form is according to relationship Eq (4): (Wang et al. 2010).

$$lnq_e = lnK_f + (\frac{1}{n})lnC_e \quad (4)$$

Where C_e is the balance concentration of DNBP, q_e the amount of pollutant absorbed on the surface, 1/n and K_f the constants in Freundlich equation. The experimental data were compared with this Isotherm in linear method and the results have been shown in Figure 7(b). According to figure, it is observed that the experimental data with fitness coefficient of 97% conforms to Freundlich equation. Also, 1/n = 0.249 and K_f= 52.08 were obtained for this process.

Given the results, it is observed that the results of DNBP surface adsorbent on the magnetic adsorbent of walnut hard-shell ashes have higher fitness with Langmuir equation and follow it. Thus, surface adsorbent of DNBP is mono-layer on this physical adsorbent. In similar studies on phenolic compounds, the consistency of the data with Langmuir equation was reported (Hameed et al., 2008; Senturk et al., 2009).

In the study by Hashemi and Colleagues into phenol removal using walnut green shell adsorbent, Langmuir and Freundlich Isotherms were also studied. Results showed that phenol adsorbent follows Langmuir model with R^2 = 0.999 (Kocer et al., 2016). A study by Pehlivan and Colleagues was reported where the walnut, hazelnut, and almond shell adsorbent were used to remove Cr (VI). The study of isotherm in this research revealed that the results for all three adsorbents were consistent with Langmuir equation and the highest capacities for Chromium adsorbent were 8.01,

8.28 and 3.40 mg/g for walnut, Hazelnut and almond shell adsorbents, respectively (Ngo et al., 2015).

Figure 7. (a) Fitness of Experimental data with Langmuir Equation and (b) Freundlich equation (adsorbent dosage = 700 mg/L and reaction time = 40 min, T = 25° C, pH = 7)

Determining the kinetics of DNBP adsorption on synthesized adsorbent

To study the kinetic of DNBP surface adsorbent process on the magnetic adsorbent of walnut hard shell ashes, the fitness of the data with two pseudo-first and second-order equations were studied under optimal conditions. The amount of material absorbed at time t per unit mass of adsorbent q_t was calculated using Eq (5):

$$q_t = \frac{C_0 - C_t}{m_{ads}} \times V \qquad (5)$$

Where C_0 is the initial concentration of DNBP in aqueous solution, C_t concentration at any moment, V solution volume in liter and m_{ads} the amount of adsorbent in gram. The data obtained for kinetic study of DNBP surface adsorbent on the magnetic adsorbent of walnut hard shell ashes were fitted with pseudo- first order Eq(6) and pseudo-second order Eq (7):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

To fit data with the pseudo- first order equation using linear method, the chart $1n(q_e-q_t)$ was drawn on the basis of time (the data was not shown). Also, Fitting data with the pseudo- second order kinetic equation was studied in linear form and t/qt was drawn on the basis of time (the data was not shown).

Given the results, it is observed that the data with correlation coefficient of 0.87 are consistent with pseudo- first order equation and with correlation coefficient of 0.99 with pseudo- second order

equation. Thus, the kinetic data in pseudo-second order model is linear and has more optimal correlation coefficient. According to results and pseudo- second order equation, the constant values of speed and DNBP absorbed in balance state are 0.00084 1/s and 29.23 mg/g, respectively. In articles presented on phenol removal using surface adsorbent method, the kinetic model of pseudo-second order has been reported for the process. (Srivastava et al., 2006; Alkaram et al., 2009).

To this end, the study by Koc er and Colleagues (Kocer et al., 2016) on the adsorbent of green Malachite using olive grounds, showed that Langmuir Isotherm model is the best Isotherm and the adsorbent kinetic was consistent with pseudo- second order equation. Also, the study by Tural and Colleagues (Tural et al. 2016) on the adsorbent of Glutaraldehyde using magnetized Nanoparticles, Chitosan has the highest consistency with Langmuir Isotherm and the adsorbent has been in mono-layer form following pseudo- second order kinetic.

CONCLUSION

Magnetic particles of walnut hard shell ashes as a natural bio-friendly and cheap adsorbent is able to efficiently remove DNBP as a toxic and persistent material from aqueous environments and industrial wastewaters. According to results of synthesized adsorbent analyses, the average pore diameter of Nanoparticles is equal to 3/3 nm and its isoelectric point is pH_{pzc}=6. Under optimal conditions, pH=7, temperature 25 ^{o} C and adsorbent 700mg, after 50 minutes, the removal efficiency of DNBP reaches around 93%; Due to the fact that the amount of phenolic compounds for discharge to surface water is allowed up to a concentration of 1 mg / l, this method is suitable for purifying contaminated water up to a concentration of 20 mg / l. Also, isotherm studies showed that the process with fitness coefficient of 0.99 follows Langmuir equation. In this process, K_L =45. 24 and a_L=0.316 and accordingly the adsorbent capacity was determined 142.88 mg/g. The kinetic results of this study showed that the process of dinitrobutyle adsorbent by magnetic adsorbent walnut hard shell ash with correlation coefficient of 0.99 follows pseudo- second order equation and

the constants of speed and the amount of DNBP absorbed in balance state is equal to 0.0084 1/s and 29.23 mg/g respectively.

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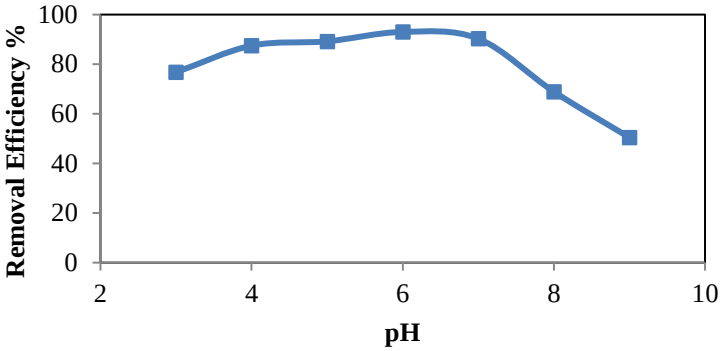

Figure 1. Effect of pH on the DNBP removal efficiency (DNBP= 20 mg/L and T= 25° C , reaction time = 50 min

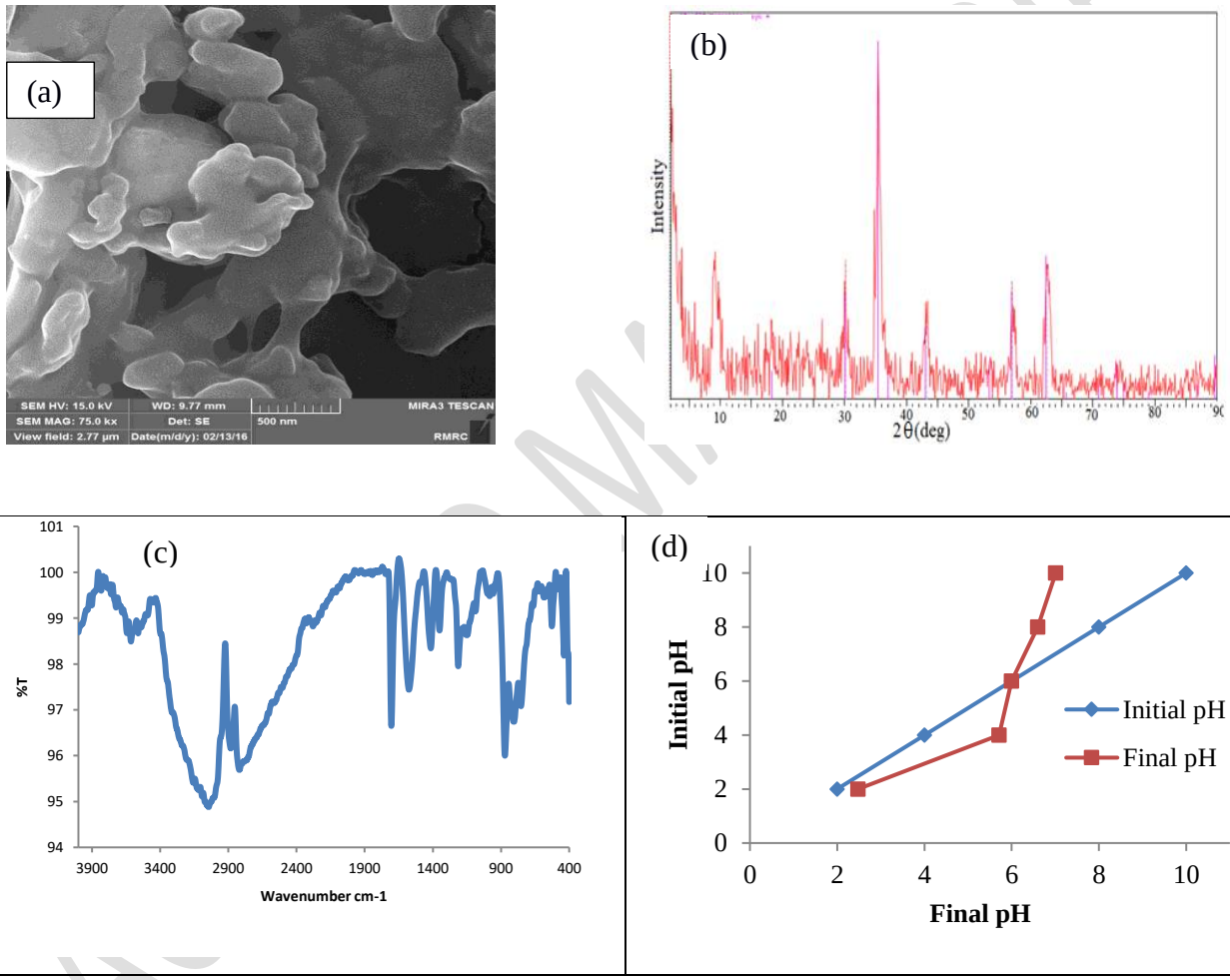

Figure 2. (a) SEM image of synthesized magnetic adsorbent, (b) XRD spectrum for magnetic adsorbent of walnut hard shell ash, (c) FTIR spectrum of magnetic adsorbent of walnut green shell, (d) point of zero charge (pH_{zpc})

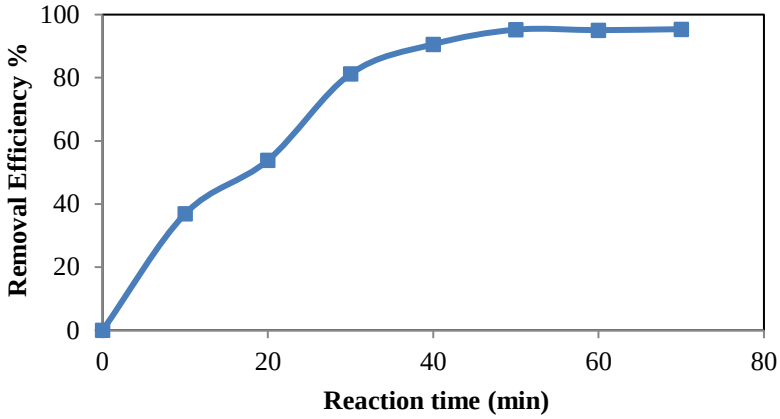

Figure 3. Changes of DNBP removal efficiency over the reaction time (DNBP concentration= 20 mg/L and adsorbent dosage = 500 mg/L, T = 25 ºC, pH = 7).

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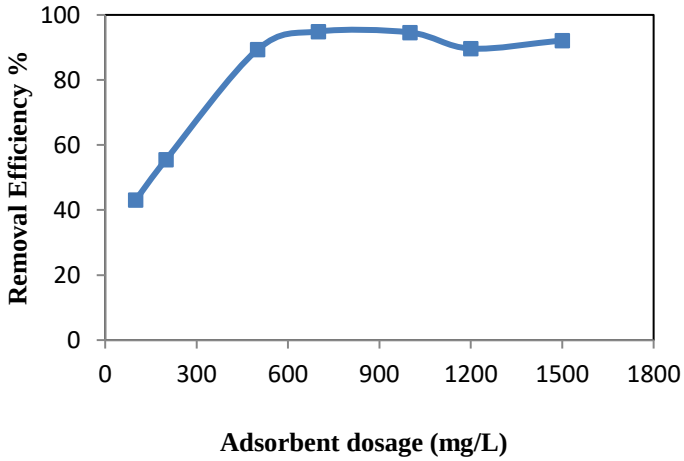


Figure 4. Effect of adsorbent dosage on the DNBP removal efficiency (T = 25º C and pH = 7, reaction time = 50 min)

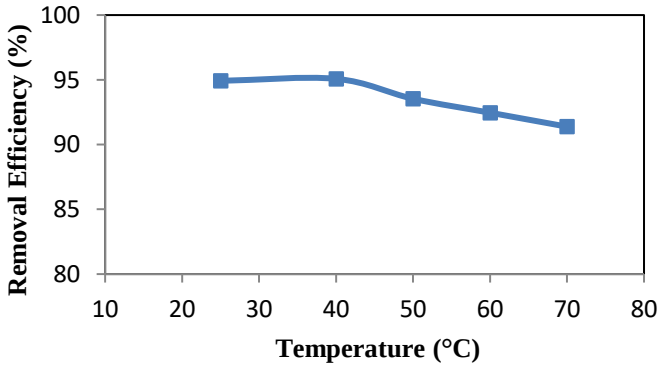
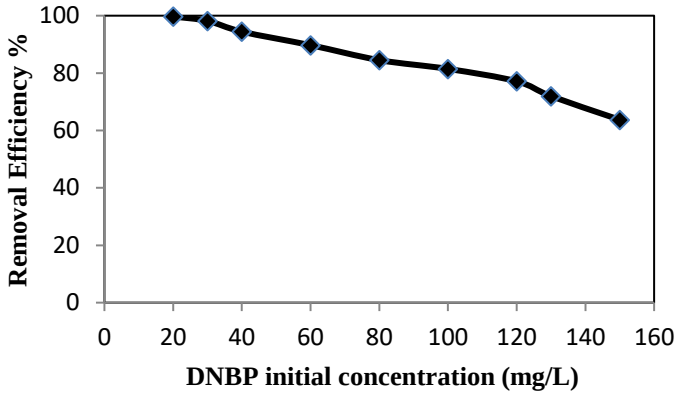


Figure 5. Effect of temperature on the removal efficiency of DNBP (adsorbent dosage = 700 mg and pH= 7, reaction time = 40 min)



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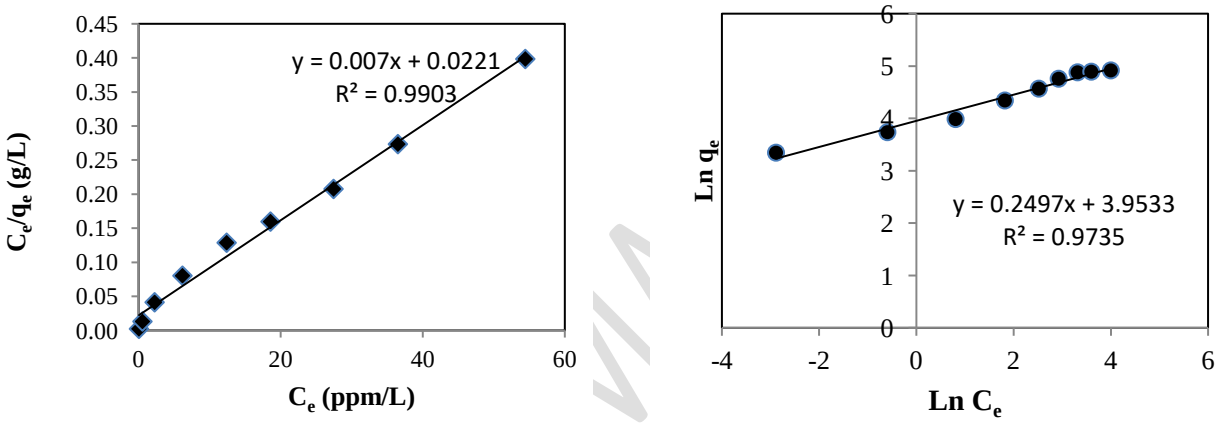
2 Figure 6. Effect DNBP initial concentration on the removal efficiency (adsorbent dosage = 700 mg reaction time, = 50
3 min, T = 25 o C, pH = 7)



4 Figure 7. (a) Fitness of Experimental data with Langmuir Equation and (b) Freundlich equation (adsorbent dosage = 700
5 mg/L and reaction time = 40 min, T = 25° C, pH = 7)

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