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Removal capability of 4-Nonylphenol using new nano-adsorbents produced in sand filters of water treatment plants

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Abstract

Sand filters are a physical treatment unit in water treatment plants that have considerable potential for removing large suspended matter. However, these filters are somewhat inefficient in removing micro-pollutants. In this study, using waste leachate, carbon nanoparticles were coated on the silica particles to increase the surface adsorption capacity on silica substrates of rapid sand filters. The surface properties of nano-adsorbents produced by scanning electron microscopy, Raman spectroscopy and EDS test were investigated. Furthermore, the adsorption capacity of 4-Nonylphenol was examined using a new nanocomposite under different operational conditions (contact time, temperature and initial concentration) and after obtaining pHzpc, the effect of pH, total dissolved solids (TDS) and total organic carbon (TOC) on the efficacy of 4-Nonylphenol removal was tested. The adsorption isotherms in three temperature amounts of 15, 25, and 50 °C were also studied and Langmuir isotherm well fit the experimental data. To evaluate the thermal effect on the adsorption process, the thermodynamic study was also conducted. The results demonstrated that this reaction is spontaneous, endothermic and thermodynamically desirable. The experimental data also showed that the new engineered material is a good reusable adsorbent in water treatment.

1. Introduction

In recent years, environmental pollution has attracted wide attention and numerous studies and articles have reported on the existence of new chemical components called emerging pollutants not only in wastewater and aquatic environment but also in sediments, soil, and atmosphere (Kanakaraju et al 2018, Zornitta et al 2020). Meanwhile, water pollution by so-called emerging pollutants has become an important environmental issue with the potential to cause adverse environmental and health effects (Geissen et al 2015, Matos et al 2019). The current knowledge is incapable of designing the water and wastewater treatment plans for filtering micro-pollutants (Schröder et al 2016, Afonso-Olivares et al 2017, Bandosz et al 2020). In other words, these plans have not been designed to remove these pollutants. The contaminants include Bisphenol A, 4-Octylphenol and 4-nonylphenol which are known as endocrine-disrupting chemicals. They have received much attention over the past decades due to their influence on the structure or function of the endocrine system (Matos et al 2019). Islam et al developed novel nano manganese oxide-based materials to remove dye from polluted water. Adsorption mechanisms investigated by various modeling approaches were also discussed (Islam et al 2019). Lee et al worked on phenol degradation catalyzed by metal oxide supported porous carbon matrix under UV irradiation. In this study, kinetic data were generated to evaluate the degradation mechanism (Lee et al 2019). Bandara et al investigated the impact of water chemistry, shelf-life, and regeneration in the removal of different chemical and biological contaminants in water using Polymeric Graphene Oxide Nanocomposite Membrane Coating. It was found that the coated filters were able to remove suspended particles, bacteria, and heavy metals effectively (Bandara et al 2019). Mostafazadeh et al developed a combined membrane filtration, electrochemical
technologies, and adsorption processes for treatment and reuse of laundry wastewater and removal of nonylphenol ethoxylates as surfactants (Mostafazadeh et al 2019). López-Pacheco et al investigated on the removal and biotransformation of 4-nonylphenol by Arthospira maxima and Chlorella vulgaris consortium. Their results suggested that microalgae and cyanobacteria consortium can be used to remove 4- nonylphenol from water (López-Pacheco et al 2019). Limmun et al also worked on the removal of nonylphenol and nonylphenol monoethoxylate from water and anaerobically digested sewage sludge by Ferrate (VI) (Limmun et al 2019). Jiang et al evaluated the potential ecological risk of residual endocrine-disrupting chemicals from wastewater treatment plants. Their results indicated that these chemicals are widely distributed in wastewater treatment plants, while nonylphenols are the predominant chemical in the effluent (Jiang et al 2020). Jawed et al reviewed the engineered nanomaterials and their surface functionalization for the removal of heavy metals. In this study, current trends of nanomaterials for the removal of heavy metals from water/wastewater were discussed and the applications of different engineered nanomaterials based on iron oxide, titanium oxide, silica, carbon, graphene oxide, and bio-nanomaterials were focused (Jawed et al 2020). Selvaraj et al also reviewed the application and prospects of carbon nanostructured materials in water treatment. They suggested that carbon-based nanostructured materials such as carbon nanotubes are considered to be the most robust and versatile candidate for the effective treatment of water (Selvaraj et al 2020). In the current study, the main focus is on the removal of 4-Nonylphenol using new nano-adsorbents.

Based on previous studies, 4-nonylphenol can be synthesized and can be removed from the water through several different purification methods such as biological (membrane bioreactors) or physical processes (membrane filtrations such as nanofiltration), biotechnological methods (biofilm), adsorption process (using common adsorbents like activated carbon or uncommon adsorbents like clay and eventually advanced oxidation processes) (Zornitta et al 2020). Nowadays, new technological advances have led to the production of new adsorbents such as nano-adsorbents which have good potential in removing contaminants (Koeppenkastrop and De Carlo 1993). However, their application in the slurry mod is somewhat problematic since they must be eliminated in the final treatment process. Furthermore, rapid sand filters are ineffective in removing 4-nonylphenol. In this regard, silica has been used which is a great natural resource and its coating with nano-adsorbents not only overcomes these problems in the slurry state but also strengthens filters and improves the filtration process. On the other hand, municipal waste collection and disposal have become one of the most important issues in integrated municipal waste management due to population growth, industrialization and consequently increasing per capita waste production (EPA 2005). The waste leachate is a complex matrix of various chemicals including soluble organic matter, mineral salts, organic impurities, and heavy metals. Each occurs at different consecration due to the physical, chemical and microbiological processes that happen in the collection centers (Jin et al 2015). This has increased the environmental hazards of waste leachate (Yang et al 2016). Using waste leachate to remove 4-nonylphenol is a good idea to turn a challenge into an opportunity.

In the present study, a new engineered nano-adsorbent was produced using waste leachate. This adsorbent was synthesized and coated on silica at the same time so that the surface of the acid-washed silica was coated with leachate and then the coated silica with the leachate is pyrolyzed at different temperatures. In the following, the optimum temperature was selected for the production of nano-adsorbents and some experiments were designed to remove 4-nonylphenol at different concentrations with different doses. Finally, the adsorption and desorption rate of the adsorbents were evaluated during seven stages.

2. Material and methods

Materials used included carbon nanotubes produced in the current study, 37 percent of hydrochloric acid, 65 percent of nitric acid, 4-Nonylphenol provided from German Merck agents, silica particles prepared from soil mechanics laboratory of engineered faculty of Tehran University and it contained 97.5 percent silica according to the manufacturer’s announcement plus other impurities such as Al₂O₃, Fe₂O₃, CaO, MgO and K₂O, and the leachate from Aradkoh Kahrizak Waste Processing and Recycling Complex (located 23 km from the old Tehran-Qom road and south Kahrizak).

-Coatings are thin layers that sit on the substrate, giving rise to new physical, mechanical, and electrical properties on the surface and thus enhancing substrate properties (Chopra and Maini 2010). In this study, the silica was firstly washed with acid to form a carbon nanotube coating on silica. The carbon nanotube was then prepared simultaneously and coated on silica and glass, and then the same method and again without coating on the substrate to prepare the engineered nano-adsorbent. Subsequently, scanning electron microscopy was used to ensure the forming of engineered nano-adsorbent. In the next step, the strength of the formed nanotubes was examined and then to investigate the adsorption effect of the three adsorbent concentration parameters (carbon...
nanotube coated on the silica particles), the adsorbed concentration (4-Nonylphenol) and the contact time were considered. Finally, carbon nanotubes were reclaimed in seven steps.

For silica washing, Fujigaya et al. method was used (Fujigaya et al. 2011). Accordingly, 500 grams of silica, 250 ml of city water, and 250 ml of 37-percent hydrochloric acid were blended and the contents were well stirred to mix thoroughly. The resulting mixture was heated at 100 °C for three hours. By doing so, the silica was washed with acid and its impurities were removed. After the washing time, the remaining silica was washed frequently with distilled water and then the water was poured out. Subsequently, the beaker containing the hydrated silica was put in a dryer at 50 °C for 24 h to dry completely. The Comparison of the washed-acid silica with raw silica indicates the clear and transparent color of silica and removal of impurities after washing.

In the next step, 500 ml of the leachate was added to 500 grams of acid wash sand and heated. The resulting mixture was being stirred constantly while being heated so that the leachate was completely in contact with the silica grains and absorbed by them. The silica-coated by leachate was then placed in the furnace to reach 100 °C at 10 min, 700 °C at 40 min and for one hour at 700 °C. Afterwards, the nano-adsorbent was taken out from the furnace and it was washed several times with distilled water after reaching ambient temperature to remove the excessive salts of the surface of the carbon nanoparticles. The entire processes of coating silica particles with leachate and pyrolysis were repeated on glass particles, as well as pyrolysis of leachate without coating on the substrate. However, to optimize the pyrolysis temperature, this process was performed at the temperatures of 300, 400, 500, 600, 700 and 800 degrees Celsius.

The sample ultrasound method was used to ensure bond strength. Ultrasonic is high-power mechanical waves that emit through new engineered nano-adsorbents samples to remove carbon nanotubes from the silica surface. In the ultrasonic bath (HWASHIN, Power Sonic 420, 50 HZ, 700 W, Seoul, Korea) with an emitted energy frequency of 40 kHz, the silica particles were exposed to ultrasonic radiation for 30 min. Low-strength carbon nanotubes were expected to be removed from the silica surface after this time, and if the bond strength was high, these particles would remain. In the high-strength silica sample, the coating did not dissipate when the silica-coated carbon nanotubes had been exposed to 40 kHz ultrasound and the apparent observation showed that no nanotubes entered the environment. Such strength was obvious from the completely transparent color of specimen containing nanotubes-coated silica. Therefore, any sample that could be used in filters needed to be previously evaluated with high ultrasonic energy. Applying ultrasonic was an indicator that could represent the bond strength after the backwash operation in the filters. It should be noted that backwash water is mainly excreted in the filters and, if a particle of carbon nanotubes is separated from the silica substrate, it is practically in the excreted water. Moreover, in refineries, this coated silica can be deposited on some filters and before the raw silica filters so that in case that any particle from the aggregated nanoparticles separates from the substrate, it gets caught in the silica-containing filters and can be removed with a backwash operation. These approaches represent solutions to strengthen the bond, although future research will be needed to pay particular attention to this issue.

After the samples have been ultrasound, the coating on the silica particles should be examined by one of the high magnification imaging techniques. For this purpose, the scanning electron microscope (KYKY EM3200, China) was used to photograph the surface of acid-washed silica and carbon nanotubes-coated samples. Moreover, the removal capacity of 4-Nonylphenol by the adsorbent produced at temperatures of 300 to 800 °C was investigated and the optimal temperature for adsorption production was determined based on the results of these experiments as well as images of scanning electron microscopy.

To investigate the removal potential of engineered nano-adsorbents (carbon nanotubes coated on silica particles), the Response Surface Methodology (RSM) and Design Expert 7.0 software tool were used. In the RSM, a set of mathematical and statistical methods is used to model and analyze processes influenced by several variables (Sadhukhan et al. 2016). Furthermore, the central composite design has been used for the design of the experiment (Myers et al. 2016). In the CCD method, based on the results of previous studies and the initial tests, an interval was determined to change the factors under investigation. Generally, three independent variables that are adsorbent concentration, sorbent concentration and contact time as well as 19 experimental points that are 8 factor points, 5 central points, and 6 axial points) were obtained. The adsorbate concentration to adsorbent concentration parameter (qe mg g⁻¹) was obtained as a response from the procedure. In this study, a comparison was made between the adsorption effect of acid-washed silica and carbon nanotube-coated silica.

To make the solution with different concentrations of 4-Nonylphenol, the initial solution was prepared with 1000 mg l⁻¹ from 4-Nonylphenol and then the required solutions were prepared at intended concentrations from the initial stock solution. Since the effect of pH value was investigated by several studies and the pH of the drinking water is in the neutral pH range, such pH value was considered. The contact time was also evaluated in the range of 2 to 40 min. The adsorbate concentration (4-Nonylphenol) in the range of 0.2–1 mg l⁻¹ and the adsorbent concentration in the range of 1 to 50 g l⁻¹ were also investigated.

To investigate the effect of TOC, TDS and pH changes on the elimination process of 4-Nonylphenol by nano-adsorbent some experiments were also performed. Since pH is one of the influential parameters in the
removal process, to investigate the effect of pH, first, the pHzpc of the new nano-adsorbent was determined by experiment and then the effect of pH on the removal of nonylphenol was investigated using pHzpc. The removal test of 4-Nonylphenol was conducted at pH of 3 to 10, the weight of sand covered with Carbon nanorods (NRs) and equals to 2.55 gr per liter, and the reaction time of 20 min with the initial concentration of 2 mg of Nonylphenol per liter. To study the effect of TOC on the Nonylphenol removal process, a solution with TOC equals to 1000 ppm was made. Then, solutions with three concentrations of 15.3, 7.5 and 3 mg l\(^{-1}\) of TOC was prepared and the experiments with the initial concentration of 2 mg l\(^{-1}\) of Nonylphenol, the adsorption rate of 2.55 g, and the contact time of 21 min were performed and the effect of Nonylphenol adsorption and the three concentrations mentioned in the TOC were also examined. To investigate the effect of TDS, groundwater with a TDS concentration of 2000 mg l\(^{-1}\) was also prepared. Then, using groundwater, experiments at concentrations of 100, 500, 1000, 1500, and 2000 mg l\(^{-1}\) of TDS with an initial concentration of 2 mg l\(^{-1}\) of Nonylphenol, an adsorbent of 2.55 g, and a contact time of 21 min were conducted. After performing the removal process, using the Nonylphenol data that remained in each sample, the TDS effect on the removal process was discussed. The adsorbate distribution between the solid phase and the aqueous solution at the constant temperature is generally represented by isotherm models (Balarak et al. 2017), and in this study, five isotherm models that are Freundlich, Langmuir, Radke–Prausnitz, Redlich–Peterson, and Dubinin–Radushkevich were used to find the best data fitting and to show the absorption performance (Chaudhry et al. 2017). Furthermore, to investigate the thermodynamic behaviors of 4-NP on NRs, the thermodynamic parameters are required. For this purpose, five different temperature amounts that are 283, 293, 303, 313, 323 °K were considered to obtain the thermodynamic parameters. Moreover, the equations (1) and (2) were used to estimate the thermodynamic parameters that are standard entropy change ΔS\(^{\circ}\) (J mol\(^{-1}\) K\(^{-1}\)), standard enthalpy change ΔH\(^{\circ}\) (kJ mol\(^{-1}\)), and Gibbs free energy change ΔG\(^{\circ}\) (kJ mol\(^{-1}\)) (Salehi and Shafie 2020).

\[ \ln K_c = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \]  
\[ \Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \]

Where R represents the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), T demonstrates absolute temperature, and k\(_c\) denotes thermodynamic equilibrium constant of adsorption. The ΔS\(^{\circ}\) and ΔH\(^{\circ}\) values are measured from the plot intercept and slope in K\(_c\) against 1/T. The negative ΔG\(^{\circ}\) values in all temperatures showed the adsorption as a spontaneous and feasible process. Furthermore, the ΔG\(^{\circ}\) spontaneous by increasing the temperatures suggests that high temperatures provide better states for absorption which means that high temperatures are optimal and favourable. The positive ΔH\(^{\circ}\) value also shows the endothermic nature of the adsorption. The positive value of ΔS\(^{\circ}\) implies increasing randomness degree at solid-liquid interface (Chaudhry et al. 2017).

Since the production of engineered nano-adsorbents requires heavy time and cost, their regeneration is very important. Particularly, the high initial cost of carbon nanotubes can greatly limit their use on real scales. For this reason and to investigate the reversibility of the adsorbed 4-Nonylphenol on the new engineered nano-adsorbent, 5 g of the engineered nano-adsorbent was approximately added to 100 ml of solution with an initial concentration of 2 mg l\(^{-1}\) of 4-Nonylphenol. After 21 min (the time of the adsorption process equilibration), the residual amount of 4-Nonylphenol was measured by HPLC. The adsorbent was then washed with methanol to remove the adsorbed particles from the adsorbent surface and reused. The desorption process was repeated at 25 °C for 7 consecutive cycles. It should be noted that in order to study the effect of methanol concentration on the regeneration of engineered nano-adsorbent, different amount of methanol concentration were used.

3. Results and discussions

3.1. Manufactured nanotubes
As mentioned in the previous section, the pyrolysis of carbon nanotubes was carried out at temperatures of 300 to 800 °C and based on scanning electron microscopy results as well as initial adsorption experiments, the temperature of 700 °C was selected as the optimum temperature for pyrolysis of carbon nanotubes. Other experiments were also performed using pyrolyzed carbon nanotubes at 700 °C. Figure 1 shows the comparative diagram of 4-Nonylphenol removal efficiency using NRs produced at different temperatures.

3.2. Images from scanning electron microscopy
Scanning Electron Microscopy was used for morphological detection of raw silica, acid-wash silica, leachate-coated silica, carbon-nanotube-coated silica, leachate-coated glass and pyrolyzed leachate at 700 °C. Figure 2 shows leachate-coated silica and carbon-nanotube-coated silica. Figure 3 shows silica coated with leachate pyrolyzed at temperatures of 300 to 800 °C. As can be seen, carbon nanoparticles formed gradually at 400 °C but they were flat and by increasing the temperature up to 700 °C, they became carbon nanotubes. However, by
increasing the pyrolysis degree temperature to 800 °C, fewer nanotubes were formed. The reason is that an increase in temperature above 700 °C can destroy the formed nanotubes. It is also observed that the surface of the coated silica contains nanotubes that are non-uniformly coated on the silica. Emitting the ultrasound waves on the specimens is the reason for the non-uniformity of the coating in which the coating was probably dropped due to their low resistance or accumulation on the silica. However, no such coating was observed on the raw silica surface.

Figure 4 (a) shows a scanning electron microscope image of the pyrolysis of leachate-coated glass particles. Although the entire coating and pyrolysis procedure of silica was precisely applied to glass particles, the nanotubes were not formed on the glass surface. Moreover, figure 4 (b) shows a scanning electron microscope image of the pyrolyzed leachate that has been heated alone in the furnace. As can be seen, the nanotubes were not formed.

3.3. Results of removal efficiency of 4-Nonylphenol using NRs

3.3.1. 4-Nonylphenol removal potential of nano-adsorbent

As discussed in section 2, the RSM and the Design Expert 7.0 software tool were used to investigate the removal potential of engineered nano-adsorbents (carbon nanotubes coated on silica particles). As can be seen in figure 5, the effect of the parameters on the adsorption process was investigated.

In figure 5 (a), the effect of time and concentration parameters was concurrently investigated, which showed that the removal percentage increased by increasing the 4-Nonylphenol concentration and time. Furthermore, as can be seen in figure 5 (b), the highest removal occurred at the minimum adsorbent concentration and maximum time. Regarding the adsorbent concentration parameter, it can be concluded that at low
concentrations the adsorbent has more capacity so that most of the sites with potential for adsorption were used. However, at high adsorbent concentrations, the rate of adsorption decreased with time. In figures 5(c) and (d), the graph shows the predicted and actual values based on the descriptive model in the RSM. According to this graph, the predicted and actual values are very close to each other.

In this study, a comparison was also made between the adsorption effect of acid-washed silica and carbon nanotube-coated silica, whose adsorption results showed that the acid-washed silica had very low adsorption capacity and in discrete experiments was less than 5 percent. However, in carbon nanotubes-coated silica at equilibrium time and the concentration of 2 mg l$^{-1}$, the adsorption capacity reached over 90 percent.

Nano-adsorbent produced in this study has advantages over other adsorbents including simple and short production steps as well as the use of waste materials that has no cost. Therefore, the cost of adsorbent production is very low. In other similar studies such as Zhao et al (2011), and Wanga et al (2017), the process of adsorbent production is very time-consuming and costly. In this study, the equilibrium time is 40 min, which is a shorter time than other nano-adsorbents. For instance, in the study of Al-Ahmari et al in which 4N-Np was
removed using hematite and goethite, the equilibrium time was 24 h or in the study of Fu et al (2016), the equilibrium time of phenol removal using GO-TiO2 and UV illumination catalyst was 480 min. In another study by Verma and Dutta (2017), the removal of 4-nitrophenol using ZG and using UV illumination catalyst had an
equilibrium time of 240 min. Moreover, in a study by Bera et al. (2016), phenol removal took 145 min to be equilibrated using HHM ZnO-G and a UV catalyst.

3.3.2. The results of the adsorption isotherms

Table 1 gives the parameters and errors calculated by five isotherm models for 4-NP adsorption. Based on the error functions and R² values, Langmuir isotherm and Redlich-Peterson model was the best one for explaining 4-NP adsorption process. As already noted, RL represents the adsorption nature. Regarding 4-NP, the RL was in equilibrium time of 240 min. Moreover, in a study by Bera et al. surface is predominantly negative. For the 4-NP

3.3.3. The results of the adsorption thermodynamic

Figure 6 represents the results of absorbance thermodynamic experiments. The negative values of ΔG° represent the adsorption process as a spontaneous and practical process. Furthermore, increasing the temperature decreased ΔG°, which shows that high temperature would provide better states for 4-NP adsorption on NRs. In fact, it indicates favorability of high temperature. In addition, positive ΔH (31.53 kJ mol⁻¹) value shows that 4-NP on NRs has a thermal nature, also revealing that ΔS° (122.37 J mol⁻¹ K⁻¹) is positive. It also indicates increasing the random degree at the liquid-solid interface.

3.3.4. The effects of pH on the 4-Nonylphenol adsorption process on NRs

The pH of the solution affects the adsorption by changing the interfacial nature of mineral/water surface through changing the ionizations of the adsorbate (via its dissociation constants pKa) and the surface functional groups of the adsorbent (via its point of zero charge, pzc).

In environmental engineering, pHpzc, i.e. pH, is of particular importance at the point where the net charge of the particle is zero. Based on previous studies, crude carbon nanotubes have a pHpzc of about 5 (Lu and Su 2007), 6.1 (Naghizadeh et al. 2013), and 6.6 (Scheibe et al. 2010). Furthermore, oxidized nanotubes have a pHpzc of about 3.1 and 3.7 (Scheibe et al. 2010). Figure 7 shows the equilibrium pH of each test material against the initial pH. The pHpzc of SiO₂ indicates that it has a positive charge at pHs below 3.4 and a negative charge at values above 3.4.

The pHpzc of NRs is 7.8, below which the surface is mainly positively charged and above pH of 7.8 the surface is predominantly negative. For the 4-NP (pKa 10.7), when the pH < pKa, the phenol end of the 4-n-NP is neutral, and when pH > pKa it becomes negatively charged. Since NRs hold a positive charge at pH < pHpzc, (which is less than the pKa 4-n-NP), the neutral end of the phenol in 4-n-NP attaches to the surface through surface physical adsorption and enhances the adsorption capacity on the NRs, as long as the pH < pKa of 4-n-NP, and pH > pzc of the NRs. When the pH of the solution approaches, the pHpzc of the NRs (pH 7–9), the surface of the NRs becomes progressively negatively charged while the 4-n-NP (as its approaches its pKa) begins to dissociate and becomes negatively charged. Due to charge repulsions between the 4-NP and negatively charged iron oxide surface, the adsorption of 4-n-NP reduces as the pH of the solution passes beyond pH 9 and approaches pH 10. The procedure is demonstrated in figure 8. Below pH 9–10, surface adsorption is predominant, and leads to stronger physical adsorption at pH values near the pKa, since this is the boundary at which the surface iron oxides are still neutral and can adsorb the 4-n-NP efficiently. Beyond pKa of 4-n-NP, the adsorption rate is reduced due to surface repulsion between the negatively charged 4-n-NP and the negatively charged NRs surface. Combining these two van de Waals repulsive forces decreases the adsorbed 4-n-NP beyond pH 9.

The tendency to enhance the adsorption rate of phenolic compounds with increasing pH has been observed with adsorption of phenols on the surface of different oxides in several studies. For instance, Zheng et al. (2007) and Chaudhry et al. (2017) suggested that the adsorption of phenol on bio-film increased gradually with pH. Wu et al. (2001) also implied that by increasing pH, the phenol uptake from polluted wastewater onto montmorillonite improved. Aksu and Yiner (1998) also concluded that there is a positive correlation with increasing pH and negative correlation with further pH increase when phenol was adsorbed in activated sludge. Nagasaki et al. (2003) studied the uptake of 4-n-NP on the surface of montmorillonite and found that the amount of adsorbed 4-n-NP increases with the increase in pH. They suggested that below the pH of 8, the deprotonation of 4-n-NP is insignificant and the adsorption of 4-n-NP onto the Na-Montmorillonite surface is only favorable. For the pH about 8, it was expected that the 4-n-NP adsorption would decrease while it was found out that the 4-n-NP adsorption continued to increase. However, they failed to explain the reason why their experiment did not follow the expected trend. In the study of Al-Ahmari et al. (2018), it was shown that an increase in 4-n-NP adsorption at pH less than the pHpzc of adsorbent (7–9) happens when the surface adsorption of the neutral 4-n-NP is on the surface of iron oxides, and a decrease in 4-n-NP adsorption at pH > pKa of NP (10.7) is due to surface repulsion from the negatively charged oxide surface. As mentioned in the results of the current research, similar results have been obtained with other studies.
| Isotherm          | Equation                                                                 | Temperature °C | R²    | RMSE  | \(\chi^2\) | Parameter | \(n_F\) | \(K_F:\text{mg g}^{-1}(\text{L mg})^{1/n}\) |
|------------------|---------------------------------------------------------------------------|----------------|-------|-------|------------|-----------|---------|---------------------------------------------|
| Freundlich       | \(\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e\)                           | 15             | 0.999 | 0.131 | 0.103      |           | 1.060  | 0.927                                       |
|                  |                                                                           | 25             | 1.000 | 0.018 | 0.002      |           | 1.056  | 1.057                                       |
|                  |                                                                           | 40             | 1.000 | 0.290 | 0.721      |           | 1.048  | 1.470                                       |
| Langmuir         | \(\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}\)               | q.e: mgL⁻¹     |       |       |            | \(m\)     |        | K_L: mg⁻¹ \(\text{L mg}^{-1}\) RL           |
|                  | \(R_L = \frac{1}{1 + K_L \times C_e}\)                                  | 15             | 1.000 | 0.116 | 0.089      | 0.189     | 5.662  | 0.72-0.98                                  |
|                  |                                                                           | 25             | 1.000 | 0.000 | 0.0000     | 0.189     | 6.447  | 0.72-0.98                                  |
|                  |                                                                           | 40             | 1.000 | 0.289 | 0.697      | 0.195     | 0.195  | 0.71-0.98                                  |
| Radke-Prausnitz  | \(\frac{C_e}{q_e} = \frac{1}{K_{RP} q_m} + \frac{C_m}{q_m}\)            |                |       |       |            | \(m\)     |        | K_{ RP}: mg⁻¹ q_m g⁻¹                      |
|                  |                                                                           | 15             | 0.954 | 0.117 | 0.084      | 0.063     | 59.306 | 0.951                                       |
|                  |                                                                           | 25             | 0.954 | 0.004 | 0.0000     | 0.059     | 37.146 | 1.086                                       |
|                  |                                                                           | 40             | 0.938 | 0.182 | 0.375      | 0.063     | 0.052  | 1.518                                       |
| Redlich-Peterson | \(\ln \left(K_g \frac{C_e}{q_e} - 1\right) = g \ln C_e + \ln \alpha_g\) | g              |       |       |            | \(g\)     |        | K_g: g⁻¹ \(\text{L mg}^{-1}\) \(\alpha_g:\text{L mg}^{-1}\)                                               |
|                  |                                                                           | 15             | 0.981 | 0.117 | 0.084      | 0.109     | 84.571 | 92.313                                       |
|                  |                                                                           | 25             | 0.981 | 0.005 | 0.0000     | 0.102     | 84.571 | 80.936                                       |
|                  |                                                                           | 40             | 0.981 | 0.287 | 0.644      | 0.088     | 84.571 | 58.200                                       |
| Dubinin-Radushkevich | \(\ln q_e = \ln q_s - \frac{\beta e^2}{\varepsilon}\)          | q_e: mgL⁻¹     |       |       |            | \(\beta:\text{mol}^{2/3}\) E:kJmol⁻¹ |
|                  | \(\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)\)              |                |       |       |            |           |        |                                              |
|                  | \(E = \frac{1}{\sqrt{2 \beta}}\)                                      | 15             | 0.980 | 0.105 | 0.636      | 1.210     | 0.000  | 2074.681                                    |
|                  |                                                                           | 25             | 0.981 | 0.040 | 0.011      | 1.316     | 0.000  | 2135.072                                    |
|                  |                                                                           | 40             | 0.983 | 0.276 | 0.276      | 1.599     | 0.000  | 2309.908                                    |
3.3.5. The effects of TDS on 4-Nonylphenol adsorption process on NRs

The results of studying the effect of TDS on the removal process 4-Nonylphenol showed that TDS changes has an insignificant effect on the removal efficiency (figure 9). It should be noted that in similar circumstances and without the presence of TDS, the removal efficiency of Nonylphenol is about 63 percent. Increasing the amount of TDS raises the amount of salt in the aqueous solution. In case that the contaminant has not acidic K (such as naphthalene), the removal efficiency is improved by increasing TDS. However, since 4-Nonylphenol has acidic
K and its solubility is low, as TDS elevates, the ionization rate of 4-Nonylphenol increases (4-Nonylphenol tends to lose H\(^+\) in the saline medium), it becomes a hydrophilic molecule, and its tendency to be absorbed on the absorbent surface will be decreased.

3.3.6. The effects of TOC on 4-Nonylphenol adsorption process on NRs

The results of experiments on the removal efficiency of 4-Nonylphenol with three concentrations of 15.3, 7.5 and 3 mg l\(^{-1}\) of TOC showed that TOC changes affected the removal efficiency so that it reduced the nitrate removal percentage from about 63 percent to about 50 percent. The results of the experiments are presented in figure 10. Increasing the amount of TOC reduces the adsorption capacity since the increase in TOC creates an adsorption competition at the surface between 4-Nonylphenol and TOC. In such a case, TOC is absorbed more to NRs, which reduces the removal efficiency of 4-Nonylphenol.

3.4. Regeneration of Engineered Nano-adsorbent

Figure 11 shows the regeneration diagram of adsorption percentage in different regeneration cycles and different concentrations of methanol, including pure methanol, 80, 60, 40, 20, and 0-percent methanol. As can be seen in figure 11, when pure methanol is used and after repeating this procedure seven times, the removal efficiency changed from 80 percent to 41 percent. The adsorption change pattern showed that the adsorption rate of 4-Nonylphenol has reached a constant level in the final cycles. These conditions can be due to the uniformity of the surface of the carbon nanotubes, which makes the adsorption distance short and there is no need to move the adsorbed material from the inner surfaces to the outer surfaces. In other words, desorption also occurs as rapid adsorption. Moreover, as can be seen in figure 11, the higher the percentage of methanol concentration, the better the regeneration of the nano-adsorbent. There is also no significant difference between the use of pure methanol and 80-percent methanol. However, when the nano-adsorbent is regenerated using zero-percent methanol (distilled water), it becomes almost ineffective.

Based on previous studies (Clark et al 2011), it is anticipated that in the future the unit cost of production of nano-adsorbents may be reduced so that the adsorption of contaminants by the nano-adsorbents become
economical. Therefore, further studies on the removal of other environmental pollutants by nano-adsorbents are strongly recommended.

4. Conclusions

Silica particles of rapid sand filters have very low potential to remove 4-Nonylphenol, but can be enhanced by coating carbon nanotubes on silica. In this study, a new engineered adsorbent was fabricated using waste leachate and carbon nanotubes on the silica surface. The coating has high strength so that the carbon nanotubes remain on the surface of the sand particles after the ultrasonic process. Scanning electron microscopy images on the coated silica demonstrated the presence of carbon nanotubes that are non-uniformly coated. The produced carbon nanotubes were then evaluated as an efficient and practical adsorbent for removal of 4-Nonylphenol from aqueous media. The results of the adsorption effect under different conditions (contact time, adsorbent and adsorbate concentration) showed that the solution reaches equilibrium at neutral pH for about 40 min. The adsorbent capacity reduces with an increase in adsorbent concentration and it expands by raising the adsorbate concentration. The results of studying the effect of TOC and TDS in water on the elimination process of 4-Nonylphenol was also indicated that TDS does not significantly affect the adsorption of 4-Nonylphenol on NRs while TOC has a negative effect on the adsorption process. Furthermore, the findings of the experiments showed that the removal of 4-Nonylphenol at neutral pH has the highest efficiency. The investigation of different isothermal absorption also indicated that the adsorption process had the best fit with Redlich-Peterson and Langmuir isotherm. Moreover, the adsorption is an endothermic, optimal, spontaneous, and disorderly process at the liquid-solid interface. In addition, the results of engineered nano-adsorbent regeneration showed the optimum condition of the adsorbent.

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