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Adsorption of 4-Chloro-2-nitrophenol onto Nano-ZnO

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Abstract

Nano-ZnO was employed for the adsorption of 4C2NP from aqueous solutions in batch equilibrium experiments to investigate its adsorption properties. The quantity of 4C2NP adsorbed onto nano- ZnO surface was measured by UV-Vis spectrophotometer. The effects of contact time, adsorbent dose, pH, and initial concentration of 4C2NP were investigated. The adsorption found to be strongly influenced by all the above parameters. The optimized conditions for maximum amount of adsorption were also determined. The results showed that adsorption of 4C2NP by nano-ZnO reached to equilibrium after 60 minutes and maximum 4C2NP removal (46.5 %) was observed at pH =6. Also, removal efficiency of 4C2NP decreased by increasing the initial concentration. Experimental data were analyzed by Langmuir and Freundlich isotherms. Experimental results indicated that the equilibrium adsorption data fitted well in the Freundlich isotherm equation with a correlation coefficient equal to 0.995.

Keywords: Nano-ZnO, 4-Chloro-2-nitrophenol, Isotherm, Adsorption, Catalyst

1. Introduction

Nitrophenols have been used in many commercial applications and entered inevitably into aquatic ecosystems [1]. These compounds are often detected as water pollutants as a result of their release in industrial effluents [2-3]. If these effluents are discharged into water without treatment, they are hazardous to humans and the environment [4]. 4-Chloro-2-nitrophenol (4C2NP), was selected as the model compound, is a recalcitrant compound and is persistent towards biodegradation. It was found in many industrial effluents, such as pesticides industrials [5]. Now there is a much need to removal of 4-chloro-2-nitrophenol that would be useful for health and environment. There are some reports to destruction of 4-chloro-2-nitrophenol such as ozonation[6], co-immobilized mixed culture system[7], various advanced oxidation processes such as UV, H_2O_2, UV/H_2O_2, Fenton, UV/Fenton and UV/TiO_2[5] and adsorption onto nano-TiO_2 [8]. It was observed that among above processes, ozonation is more effective to degradation of 4C2NP and is completely degraded it after 60 minutes. Therefore, ozonation is an effectiveness process but the practical use of ozonation for treatment of pollutants is limited by its high-energy demand [9]. Nowadays, the researcher are tried to find a simple and easy method for removal of pollutants. Adsorption of compounds on to the surface of catalysts especially nano catalysts is a simple and interesting method to removal of pollutants

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from aqueous solutions. The large of nanostructures such as TiO_2 , ZnO, MgO, CaO and etc have been extensively studied to adsorb of organic pollutants from water [10-11]. The advantage of using these inorganic oxides is that they contain environmentally safe mineral elements essential to humans and exhibit strong activity even when administered in small amount.

The nanosized ZnO due to the higher surface-to-volume ratio, high ultraviolet (UV) absorption, long life-span [12], high oxidative capacity, low cost, high chemical stability and low toxicity [13] has been widely used as catalyst [14-15], gas sensor [16-17], active filler for rubber and plastic, UV absorber in cosmetics and anti-virus agent in coating [18–19]. It also offers some advantages over TiO_2 that ZnO can simultaneously sense and destroy pollutants [20-23]. The aims of this study is to investigate the effect of different parameters such as contact time, pH, adsorbent dose and initial 4C2NP concentration on the adsorption of 4C2NP onto nano-ZnO surface from aqueous solution and find optimum adsorption isotherm.

2. Experimental

Materials

The chemical 4-chloro-2-nitrophenol (4C2NP) [$C_6H_{14}NO_3Cl$, M=173.56] (Fluka Co., Germany) was selected as a model compound. A stock solution of 4C2NP was prepared in deionized water (Millipore Milli-Q water) at a concentration of approximately 10 mg/L. All solutions were prepared using deionized water. Nanosized ZnO was supplied from Aldrich (USA). Its diameter was <100 nm and its surface area (15-25 m^2/g) was determined by a BET surface area analyzer. All other chemicals such as hydrochloric acid, hydroxide sodium and etc were reagent grades and were supplied from Merck, Germany.

Procedure

All of the adsorption experiments were conducted in a 1000 ml erlyn mayer on the magnetic stirrer. The variation of the 4C2NP concentration versus time in the aqueous solution was monitored under various conditions such as nano-ZnO dosage (0.05, 0. 1, 0.15 and 0.2 g), initial pH (2, 4, 6, 8, 10 and 12) and initial 4C2NP concentration (0.5, 1, 1.5, 2, 4, 6, 8 and 10 mg/L). The pH of the solution was adjusted using HCl and NaOH. In all of the experiments, samples were taken at predetermined time intervals (each 10 min). Following sampling, the suspensions were centrifuged (Model CE.148, Shimifan, Iran) at 8000 rpm for 10 min for subsequent analysis of the 4C2NP concentration, using UV-Vis spectrophotometer (Model DR-5000, Hach, USA). Absorbance was measured at a wavelength of 234 nm (λ_{max} for basic and neutral conditions) and 220 nm (λ_{max} for acidic conditions).

The adsorption yield (%), the adsorbed 4C2NP amount onto the ZnO nanoparticles (mg/g) at any time (q_t) and at equilibrium (q_e), were calculated from the following equations (1-3), respectively:

$$\text{Adsorption yield}\ (\%) = \frac{C_t - C_0}{C_0} \times 100 \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)}{M} V \qquad (2)$$

$$q_e = \frac{(C_0 - C_e)}{M} V \qquad (3)$$

where C_0, C_t and C_e are the initial, at any time and equilibrium 4C2NP concentration (mg/L), respectively. V is the solution volume (L) and M is the adsorbent mass (g).

3. Results and Discussion

Effect of contact time

Adsorption of 4C2NP increases with increase in contact time (Fig. 1) and reaches the equilibrium within 60 min. The removal of 4C2NP by adsorption onto nano-ZnO was initially fast and then slows down with increasing contact time.

Effect of adsorbent

The effect of catalyst weight on the adsorption of the 4C2NP was studied in the range of 0.05, 0.1, 0.15 and 0.2 g. Fig. 2 shows a percent of the 4C2NP adsorbed by nano-ZnO as a function

of contact time. As shown, the adsorption of 4C2NP increased with increasing adsorbent dose from 0.05 g to 0.1 g due to increase of surface area available for adsorption [24]. Further increase in nano- ZnO weight resulted in the decrease of the capacity as shown in Fig. 2. This reduction had been explained as due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles above 0. 1 g [25]. In fact, 4C2NP uptake was significantly higher when the dosage was 0.1 g. So, the optimum of nano ZnO was 0.1 g in subsequent experiments of this work.

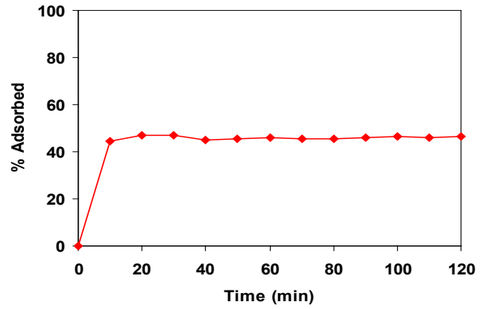

Fig. 1. Effect of contact time on the adsorption of 4C2NP onto nano-ZnO $[4C2NP]_0$ = 10.0 mg/L;$[ZnO]_0$=0.1 g; pH: 5.64; temperature= 25 ^{0}C

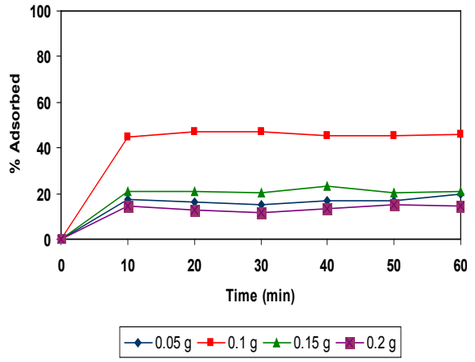

Fig. 2. Effect of adsorbent dosage on the adsorption of 4C2NP onto nano-ZnO $[4C2NP]_0$ = 10.0 mg/L; pH: 5.64; temperature= 25 ^{0}C

Effect of initial pH

The pH is an important factor controlling the adsorption process. To study the effect of pH on the adsorption of 4C2NP, pH of solution is adjusted in the range 2–12. The experimental conditions were 10 mg/L of 4C2NP and 0.1 g of nano-ZnO. Fig. 3 shows the effect of pH on the adsorption of 4C2NP. The adsorption of 4C2NP after 10 min were 24.22, 31.60, 44.69,17.92,12.88 and 4.27% for pH=2,4,6,8,10 and 12, respectively. Based on the results, the adsorption of 4C2NP onto nano-ZnO was high at acidic conditions and the optimum pH is 6. The effect of pH on the adsorption of 4C2NP onto nano-ZnO can be explained by taking into consideration the surface area of catalyst. High adsorption of 4C2NP in acidic condition may be due this fact that nano particles of metal oxides when suspended in water, formed aggregate [26]. As reported nano-ZnO particles enlarged above pH >6.5 and about pH 7.5, the size of the ZnO reaches up to 350 nm[27]. So, the surface area is decreased and the adsorption is dropped.

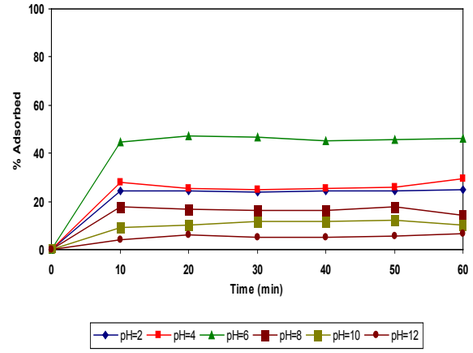

Fig. 3. Effect of pH on the adsorption of 4C2NP onto nano-ZnO, $[ZnO]_0$=0.1 g; $[4C2NP]_0$ = 10.0 mg/L; temperature= 25 ^{0}C

Effect of 4C2NP concentration

The influence of 4C2NP concentration on adsorption of 4C2NP at different contact time onto nano-ZnO particles, at 25 ˚C, was investigated in the range of 0.5, 1, 1.5, 2, 4, 6, 8 and 10 mg/L by using 0.1 g of the adsorbent. The results presented in Fig. 4 show that in low concentrations of 4C2NP (0.5-2 mg/L), the percentage of adsorption was increased and then decreased with increasing initial 4C2NP concentration (2-10 mg/L). Based on results, when the initial 4C2NP concentration increased from 0.5 to 2 mg/L, the amount of 4C2NP adsorbed increased from 16.80 to

49.13%. This is obvious from the fact that the initial 4C2NP concentration provides an important driving force to overcome all of mass transfer resistance [8]. The lower uptake at higher concentration resulted from an increased ratio of initial adsorption number of moles of the 4C2NP to the available surface area; hence fractional becomes dependent on initial concentration. For a given adsorbent dose the total number of available adsorption sites is constant. Thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration (saturation of the adsorbent) [28-29].

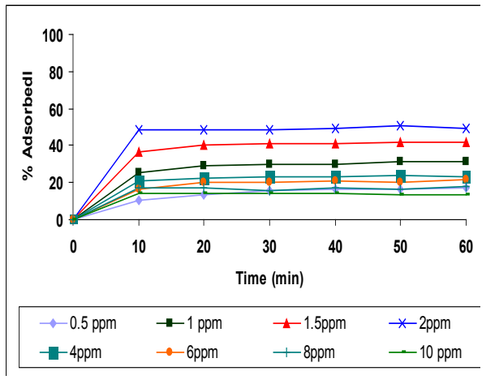

Fig. 4. Effect of initial 4C2NP concentration on the adsorption of 4C2NP on nano-ZnO, $[ZnO]_0$=0.1 g; pH: 5.64; temperature= 25 ^{0}C

Equilibrium isotherms

The adsorption isotherm describes how adsorbate molecules interact with adsorbents when the adsorption process approaches to an equilibrium state. Equilibrium adsorption isotherm data were analyzed according to Langmuir and Freundlich models. The well-known expression of the Langmuir model is [30],

$$\frac{1}{q_e}=\left(\frac{1}{K_L q_m}\right)\frac{1}{C_e}+\frac{1}{q_m}$$

whereq_e (mg/g) and C_e (mg/dm^3) are the amount of adsorbed 4C2NP per unit weight of sorbent and unadsorbed 4C2NP concentration in solution at equilibrium, respectively. q_m (mg/ g) is the Langmuir constant representing maximum monolayer capacity and K_L is the Langmuir constant related to energy of adsorption. The values of q_m and K_L are calculated from the intercept and slope of the linear plot of 1/q versus 1/C.

Freundlich isotherm model is described as [31]:

$$Lnq_e=\left(\frac{1}{n}\right)LnC_e+LnK_F$$

Where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

When performing data fitting, linear regression is generally used to determine the parameters of isotherm models. Langmuir and Freundlich plots based on the experimental data are presented in Figs. 5 and 6. It was found that Freundlich model provides a better behavior of the residuals, and suitable value of R^2 is obtained for Freundlich (0.995) than langmuir (0.890). This revealed the data were better fitted to the Freundlich equation than Langmuir equation. So, the adsorption of 4C2NP onto nano-ZnO was correlated well with the Freundlich equation under the concentration range studied. The parameter *n* in the Freundlich equation is an indicative of the sorption intensity. If *n* lies between one and ten, this indicates a favorable sorption process [32]. Since the calculated value of n in this research is 4.4, this indicates favorable 4C2NP adsorption by nano-ZnO.

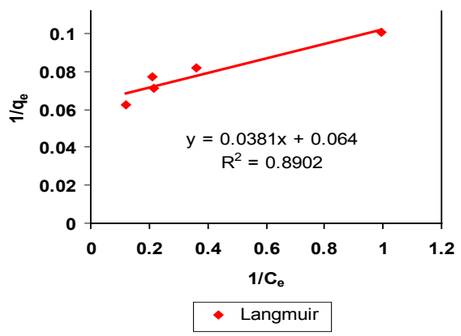

Fig. 5. Langmuir isotherm for 4C2NP adsorption onto nano-ZnO

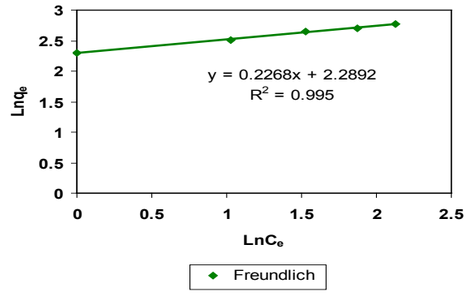

Fig. 6. Freundlich isotherm for 4C2NP adsorption onto nano-ZnO.

4. Conclusion

From the current study we can conclude that 4C2NP can be relatively removed by nano-ZnO from aqueous phase. The maximum adsorption was attained within 60 minutes and the optimum pH for the adsorption of 4C2NP was found to be at 6.0. In comparison the results of adsorption of 4C2NP onto nano-TiO_2 (about 25%), nano-ZnO improved the removal of 4C2NP (%46). The Langmuir and Freundlich adsorption isotherm models were used to express the adsorption phenomenon of the 4C2NP. The equilibrium data were well described by the Freundlich model.

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