Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://jca.edu.vn

Adsorptive removal of organochloride pesticide in water using surfactant modified aluminum hydroxide nanoparticles

Thi Hang Nguyen[1,2], Duy Tung Vu[1], Minh Ngoc Nguyen[1], Thi Anh Huong Nguyen[1], Thanh Son Le[1], Tien Duc Pham[1,*]

[1]Faculty of Chemistry, University of Science, Vietnam National University, Hanoi, 19 Le Thanh Tong, Hoan Kiem, Hanoi, Vietnam
[2]Department of Infrastructure and Urban Environmental Engineering, Hanoi Architectural University; Nguyen Trai, Thanh Xuan, Hanoi, Vietnam
**Email: tienducpham@hus.edu.vn*

ARTICLE INFO

Received: 20/10/2023
Accepted: 15/12/2023
Published: 30/3/2024

Keywords:
DDT, adsorption, α-$Al(OH)_3$, water treatment

ABSTRACT

In the present study, an anionic surfactant, sodium dodecyl sulfate (SDS) was used to modify aluminum hydroxide nanoparticles to form a novel adsorbent (SMAH) for removal of an organochloride pesticide, Dichlorodiphenyltrichloroethane (DDT) in water environment. The DDT removal using α-$Al(OH)_3$ and SMAH nanoparticles were 35.5, and 96.1 %, respectively indicated the high removal efficiency of SMAH compared with α-$Al(OH)_3$. The effective conditions for adsorptive removal of DDT using SMAH were optimized and found as pH 8, contact time 30 min and SMAH dosage 25 mg/mL. The maximum adsorption capacity of DDT on SMAH calculated by a two-step model was found to be 2500 µg/g. After five regenerations, the DDT removal was still higher than 80 %. Adsorption isotherms of DDT on SMAH and the surface charge change of SMAH after adsorption demonstrate that hydrophobic interactions in the presence of SDS bilayer of admicelle is the main driving force to control DDT adsorption on SMAH.

1. Introduction

Pesticides are the important chemicals that are widely used in agricultural activities. However, many pesticides are the persistent organic pollutants (POPs) according to Stockhom convention in 2001. Dichlorodiphenyltrichloroethane (DDT) which belongs organochloride pesticides (OCPs), is an emerging POPs that should be removed due to very stable and dangerous to human health [1]. Similar to lindane, DDT can accumulate in biocells of humans and animals [2]. The DDT residual in water is still a serious concern due to its very low biodegradation. Recently, various techniques were developed for removal of DDT and OCPs including biodegradation [3], photocatalysis [4], coagulation/ flocculation [5] and adsorption [1, 6, 7]. Among them, adsorption is an effective, simple and low-cost technique for OCPs removal [1, 8] when using the natural or waste adsorbents. The DDT is a hydrophobic compound, thus an increase the hydrophobicity of adsorbent is a great of importance to enhance removal efficiency [3, 7].

Aluminum hydroxide and aluminum oxide are common adsorbents in environmental chemical engineering [9, 10]. In our previous studies, alpha aluminum hydroxide, α-$Al(OH)_3$ was modified by both anionic surfactant,

https://doi.org/10.62239/jca.2024.004

sodium dodecyl sulfate (SDS) [11] and cationic surfactant, cetyltrimethylammonium bromide (CTAB) [8] to remove lindane from aqueous solution with very high efficiencies. The SDS modified aluminum hydroxide (SMAH) is more effective than CTAB modified aluminum hydroxide (CMAH) in the lindane removal. The reason for the high effectiveness of SMAH in removal of hydrophobic substance is due to the presence of bilayer micellization (admicelles) for SDS could be easily formed than CTAB. To emphasize the performance of SMAH in the removal of hydrophobic OCPs, another systematical study on removal of DDT using SMAH is necessary. Therefore, in this wok, we investigate adsorptive removal of DDT using SMAH in water environment.

2. Experimental

Materials

The α-$Al(OH)_3$ nanoparticles were synthesized by the precipitation method according to the procedure in our previous paper [8]. In the paper [8], the α-$Al(OH)_3$ nanoparticles were thoroughly characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX), Brunauer–Emmett–Teller (BET) and zeta potential measurements. Dichlorodiphenyltrichloroethane (DDT), an analytical reagent with high purity of 99%, was purchased form Sigma-Aldrich. Sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl), and other chemicals were also delivered from Scharlau, Spain. Ultra-pure water was used to prepare all aqueous solutions. A pH meter (HI 2215, Hanna, USA) was used to monitor all pH of solutions.

Preparation of SDS modified α-$Al(OH)_3$ (SMAH)

A solution of 100 mM SDS was mixed with 2 mL suspension of 100 mg/mL α-$Al(OH)_3$ nanoparticles in the presence of 100 mM NaCl solution. Then, the solutions were adjusted to pH 4 before filling by ultrapure water to 10 mL in 15 mL Falcon tubes to form SDS modified α-$Al(OH)_3$ (SMAH) [11].

Adsorption study

A 100 µg/L of DDT was mixed with SMAH adsorbent in 15 mL Falcon tubes. After that, the pH solutions were adjusted to given values before shaking for various contact time. To find optimum conditions including contact time, pH and SMAH dosage were systematically studied by changing one parameter while the other conditions were fixed. The triplicated experiments were conducted for all adsorption studies.

Adsorption isotherms were carried out under optimum conditions. The suspensions were centrifuged by using a refrigerated centrifuge (MR23i, JOUAN, France) at 10.000 rpm for 10 min. The DDT concentrations were determined by GC-ECD with Scion 456GC coupling with an autosampler CP-8400 (Bruker). A DB-5 (5% phenyl and 95% methyl polysiloxane) capillary column of 30 m x 0. 25 mm x 0.25 µm was used to separate DDT in the GC system. The Nitrogen gas (99.99%) with a flow rate of 1.2 mL/min was used as mobile phase. The ECD detector temperature of 300 °C and injector temperature of 250 °C with splitless mode were used.

The removal efficiency (%) of DDT was determined by the following equation:

$$Removal\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i (µg/L) and C_f (µg/L) are initial and final concentrations of DDT, respectively.

The adsorption capacities of DDT on SMAH were calculated by using the equation:

$$\Gamma = \frac{C_i - C_e}{m} \times 1000 \ (2)$$

where Γ is the adsorption capacity of DDT (µg /g), Ce is the equilibrium concentration of DDT (µg /L), and m is the adsorbent dosage (mg/mL).

Adsorption isotherm of DDT on SMAH were fitted by a two-step model using a general isotherm equation. The general isotherm equation is:

$$\Gamma = \frac{\Gamma_\infty k_1 C\left(\frac{1}{n} + k_2 C^{n-1}\right)}{1 + k_1 C(1 + k_2 C^{n-1})}$$

where C is the DDT equilibrium concentrations of, Γ is the amount of adsorbed DDT at concentration C, Γ_∞ is the maximum adsorption capacity, k_1 and k_2 are equilibrium factors involved in the first and second step, respectively, and n is clusters of the adsorption layer. The surface charge changes by monitoring ζ potential of α-$Al(OH)_3$ after SDS modification and DDT adsorption were determined by a Zetasizer Nano ZS (Malvern, England) by Smoluchowski's equation using the electrophoretic mobility measurements [12].

3. Results and discussion

Adsorptive removal of DDT using α-$Al(OH)_3$ and SMAH

The 100 mM SDS was used to modify the surface of nano α-Al_2O_3 in 100 mM NaCl at pH 4. The SDS adsorption on α-$Al(OH)_3$ at pH lower than point of zero charge (PZC) is governed by both electrostatic and hydrophobic interactions at high ionic strength. As a result, the surface charge of α-$Al(OH)_3$ is negative in the presence of micelles which can enhance DDT adsorption.

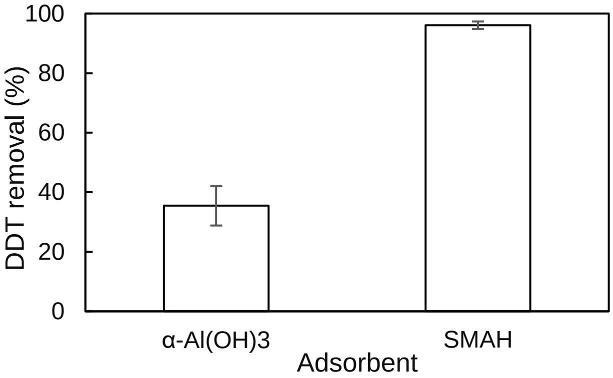

Fig. 1: Adsorptive removal of DDT removal using α-$Al(OH)_3$ and SMAH. Error bars show standard deviations of triples

Figure 1 shows that the DDT removal efficiencies in 10mM NaCl (pH 8) increased from 35.5 to 96.1 %. when using α-$Al(OH)_3$ and SMAH. The significant increase in removal suggests that SMAH is much more effective than α-$Al(OH)_3$. Thus, we only investigate the DDT removal using SMAH in the further studies.

Adsorption of DDT using SMAH

Effect of contact time

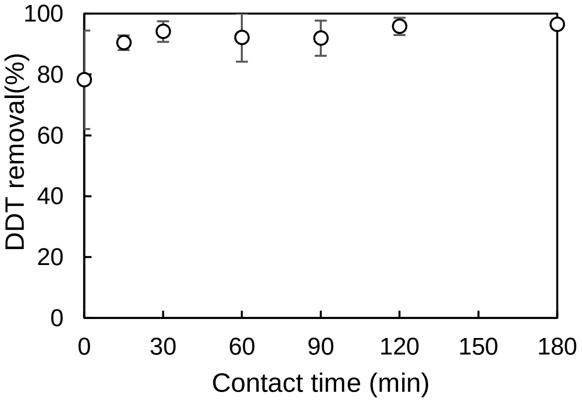

Fig. 2: Effect of contact time on DDT removal using SMAH (C_{DDT} = 200 μg/L, pH 8, and SMAH dosage 25 mg/mL). Error bars show standard deviations of triples

Contact time affects to the equilibria of adsorption process. The removal of DDT using SMAH was carried out with initial DDT concentration of 200 μg//mL in 10 mM NaCl (pH 8) whereas the contact time was changed from 0 to 180 min.

Figure 2 shows that DDT removal using SMAH increased significantly from 0 to 30 min and reached the plateau quickly. After 30 min, DDT removal changed insignificantly because adsorption equilibrium was taken place. The contact time in the present study is 2 times shorter than OCPs pesticides removal using bagasse fly ash [1]. Thus, contact time of 30 min is selected for DDT using SMAH.

Effect of pH

The pH is always an important factor in adsorption process because pH may induce the charging property of SMAH adsorbent, while the charging behavior of DDT is not strongly depended on pH. The pH effect was studied in the range of 3.0-11.0.

Figure 3 indicates that the DDT removal using SMAH fluctuated slightly in all pH range 3.0 -11.0 although at low and high pH values the DDT removal efficiencies were lower than that at neutral pH due to the desorption of SDS [13]. At pH 8, DDT removal using SMAH achieved the highest efficiency so that the optimum pH for DDT removal using SMAH was 8.0. It should be noted that α-$Al(OH)_3$ did not change the structure form at pH > 7.0 although SDS desorption was occurred at high pH [13].

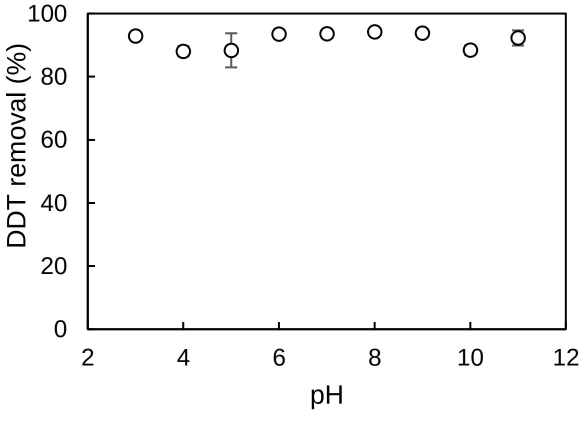

Fig. 3: Effect of pH on DDT removal using SMAH (C_{DDT} = 200 μg/L, contact time 30 min, and SMAH dosage 25 mg/mL). Error bars show standard deviations of triples.

Effect of adsorbent dosage

Adsorbent dosage influences to total site and specific surface area for adsorbate uptake. Figure 4 shows that the DDT removal using SMAH increased when the dosage increases from 0.1 to 25 mg/mL. When

https://doi.org/10.62239/jca.2024.004

increasing SMAH dosage than 25 mg/mL, the DDT removal changed insignificantly because the surface sites were enough for adsorption. Therefore, 25 mg/ mL SMAH is selected as optimum dosage for DDT removal.

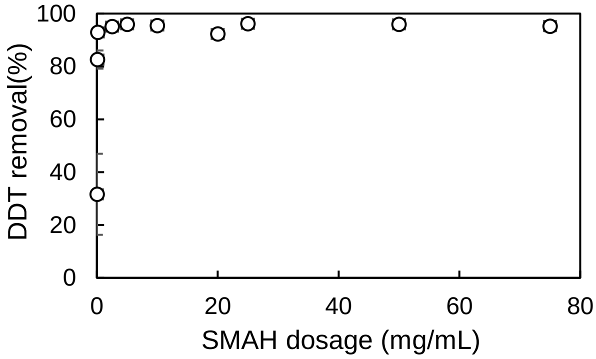

Fig. 4: Effect of SMAH dosage on DDT removal (C_{DDT} = 200 µg/L, pH 8, and contact time 30 min). Error bars show standard deviations of triples

Adsorption isotherms of DDT on SMAH

Adsorption isotherms of DDT on SMAH at two NaCl concentrations were performed under optimum adsorptive conditions of contact time 30 min, pH 8 and adsorbent dosage 25 mg/mL. The initial concentrations of DDT were prepared from 100 to 5000 µg/L. A two-step adsorption model with general isotherm equation [14] was used to fit experimental data of DDT adsorption capacity as the function of equilibrium concentrations shown in Table 1.

As can be seen in Table 1, DDT adsorption capacity increased 2 times from 1250 to 2500 µg/g with an increase of NaCl concentration from 1 to 10 mM. The maximum adsorption capacity in our case is higher than many reported adsorbents [5, 15]. The values of $k_{1, DDT}$ and $k_{2,DDT}$ also increased about 4.0 and 2.4 times, respectively while n_{DDT} decreased 1.5 times when increasing ionic strength 10 times. It should be noted that an increase ionic strength causes a decrease in electrostatic interaction. However, hydrophobic interaction was increased with increasing ionic strength could promote the adsorption.

Table 1: The adsorption isotherms of DDT on SMAH at two NaCl concentrations fitted by two-step model

C_{NaCl} (mM)	Γ_{DDT} (µg/g)	$k_{1, DDT}$ (g/µg)	$k_{2, DDT}$ (g/µg)$^{n-1}$	n_{DDT}
1	2500	0,333	584785	1.5
10	1250	1,33	1390258	1.0

The adsorption mechanism of DDT on SNAH is also discussed on the basis of surface charge change by ζ potential (not shown in detail). The ζ potential of α-$Al(OH)_3$, changed from positive (ζ = 24.1 mV) to negative with low value (ζ = -2.4 mV) at pH 8 because SDS is a strong anionic surfactant. However, after DDT adsorption due to strong hydrophobic interaction between hydrocarbon chains of DDT and bilayer of SDS admicelles of SMAH, the negative charge of SMAH changed to small positive (ζ = 1.96 mV).

The results of adsorption isotherms and the ζ changes after adsorption demonstrate that DDT adsorption on SMAH is mainly controlled by hydrophobic interactions between aromatic rings of DDT and alkyl groups of SDS micelle that is similar to the case of lindane adsorption on SMAH [11].

Regeneration of adsorbent

The regeneration of adsorbent is important to demonstrate the reuse potential and performance of adsorbent.

Due to the strong interaction between DDT and SMAH, we used 2 M NaOH to desorb DDT until the DDT concentration couldnot detect by GC-ECD. After that, the adsorbent was remodified with SDS residue under the optimum conditions. To confirm the unchanged adsorbent dosage, we compared the mass of adsorbent dosage in solution before and after regenerations. The differences after regenerations were insignificant. The DDT removal efficiencies reused SMAH are indicated in Fig. 5.

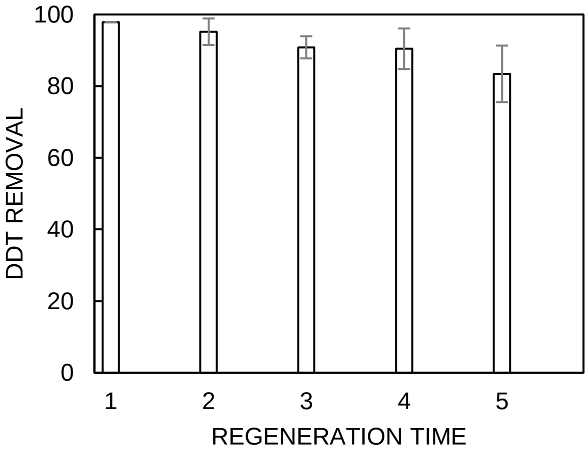

Fig. 5: The DDT removal using SMAH after five regenerations. Error bars show standard deviations of triples

Figure 5 shows that the DDT removal efficiencies using SMAH after five regenerations were decreased slightly and reached about 83.4 %. There results again demonstrate that SMAH is reusable and effective adsorbent for DDT removal in aqueous solution.

4. Conclusion

We have investigated adsorptive removal of DDT using SDS modified α-$Al(OH)_3$ (SMAH). The DDT removal using SMAH increased about 2.7 times compared to α-$Al(OH)_3$. The optimum conditions for DDT removal of DDT using SMAH were found to be contact time 30 min, pH 8, and SMAH dosage 25 mg/mL. Adsorption isotherms of DDT on SMAH were fitted well by a two-step model. The maximum adsorption capacity of DDT on SMAH reached to 2500 μg/g. After five reused times, the DDT removal was higher than 83.4 %, indicating that SMAH is a high performance adsorbent. Based on adsorption isotherms of DDT on SMAH and the ζ change of SMAH after DDT adsorption, we conclude that DDT adsorption on SMAH was controlled by hydrophobic interaction than electrostatic interaction.

Acknowledgement

This research was funded by the research project QG.22.75 of Vietnam National University, Hanoi.

References

1. Gupta VK, Jain CK, Ali I, Chandra S, Agarwal S. Water Res 36 (2002) 2483-90. https://doi.org/10.1016/S0043-1354(01)00474-2.
2. Sarkar SK, Bhattacharya BD, Bhattacharya A, Chatterjee M, Alam A, Satpathy KK, Jonathan MP. Environment International. 34 (2008) 1062-10771. https://doi.org/10.1016/j.envint.2008.02.010.
3. Liyan S, Youcai Z, Guojian W, Bing L, Dongjie N, Xiaoli C. Journal of Hazardous Materials 146 (2007) 289-294. https://doi.org/10.1016/j.jhazmat.2006.12.041.
4. Khan S, Han C, Sayed M, Sohail M, Jan S, Sultana S. Catalysts 9 (2019) 425.
5. Jemal T, Astatke H, Terfe A, Mekonen S. PLOS ONE 18 (2023) e0288086. https://10.1371/journal.pone.0288086.
6. Mojiri A, Zhou JL, Robinson B, Ohashi A, Ozaki N, Kindaichi T, Farraji H., Vakili M. Chemosphere 253 (2020) 126646. https://doi.org/10.1016/j.chemosphere.2020.126646.
7. Sprynskyy M, Ligor T, Buszewski B. Journal of Hazardous Materials 151 (2008) 570-577. https://doi.org/10.1016/j.jhazmat.2007.06.023.
8. Nguyen TH, Nguyen TTL, Nguyen TC, Doan TH, Le QH, Bui QM, Le TS., Pham TD. Materials Today Communications 34 (2023) 105266. https://doi.org/10.1016/j.mtcomm.2022.105266.
9. Pham TD, Kobayashi M, Adachi Y. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 436 (2013) 148-157. http://dx.doi.org/10.1016/j.colsurfa.2013.06.026.
10. Franks GV, Gan Y. Journal of the American Ceramic Society 90 (2007) 3373-88. https://10.1111/j.1551-2916.2007.02013.x.
11. Nguyen TH, Nguyen TTL, Pham TD, Le TS. Polymers. 12 (2020) 960.
12. Delgado AV, González-Caballero F, Hunter RJ, Koopal LK, Lyklema J. Journal of Colloid and Interface Science 309 (2007) 194-224.
13. Yen Doan TH, Hoang TH, Le VA, Vu DN, Vu TN, Srivastav AL, Pham TD. Environmental Research. 216 (2023) 114618. https://doi.org/10.1016/j.envres.2022.114618.
14. Zhu B-Y, Gu T. Advances in Colloid and Interface Science 37 (1991) 1-32. https://dx.doi.org/10.1016/0001-8686(91)80037-K.
15. Ormad MP, Miguel N, Claver A, Matesanz JM, Chemosphere 71 (2008) 97-106. https://doi.org/10.1016/j.chemosphere.2007.10.006.