Adsorption of Zn, Cd and Mn Ions onto Purified and Functionalized CNTs from Pharmaceutical Wastewater

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ABSTRACT

The continuous discharge of industrial influent into the environment causes harmful effects in the surrounding ecosystem due to the inherent chemicals. This study is focused on the removal of heavy metals from pharmaceutical wastewater using a carbon nanotube adsorbent (CNTs). Carbon nanotubes were produced using bimetallic Fe-Co catalyst supported on kaolin via wet impregnation technique. Carbon nanotubes were synthesized through catalytic chemical vapour deposition and purified with acid treatment to give P-CNTs. The purified CNTs were functionalized with polyethylene glycol to give F-CNTs. The catalyst, P-CNTs and F-CNTs were characterized by Brunner-Emmett-Teller (BET), High Resolution Transmission Electron Microscope (HRTEM) and High resolution Scanning Electron Microscopy (HRSEM). Specific surface area obtained for F-CNTs and F-CNTs were 657.56 and 867.23 m^2/g respectively. The HRSEM depicts the cluster nature of the produced CNTs while the HRTEM depicts the internal and external diameter of 21.62 and 43.60 nm respectively. The F-CNTs and F-CNTs adsorbents were used for the removal of heavy metals (Zn, Cd and Mn) from pharmaceutical wastewater. The influence of contact time, temperature and adsorbent dosage were investigated on the nano-adsorbents. F-CNTs exhibited the most suitable results compared to P-CNTs with optimum conditions of 60 minutes contact time, 0.3 g adsorbent dosage and temperature of 60°C with percentage removal of 89.78, 94.65 and 93.32 % for Zn, Cd and Mn respectively on to F-CNTs. Freundlich isotherm was more fitted to the adsorption data than the Langmuir isotherm. Pseudo-second order kinetic model best describes the adsorption behavior, and the thermodynamic studies showed the spontaneity and endothermic nature of the reaction process. The study shows that the functionalized carbon nanotubes produced has the affinity to remove Zn, Cd and Mn ions from pharmaceutical wastewater.

Keywords: Adsorption, Functionalization, MWCNTs, cobalt-ferrites and Pharmaceutical Wastewater

INTRODUCTION

Heavy metals are naturally occurring elements present in varying concentrations in the environment. They are categorized as metals because they all have specific density greater than 5 g/cm^3 which can cause severe harm to living organisms, and to the environment at large (Jaishankar *et al.*, 2014). Some of the frequent found heavy metals in wastewater include cadmium, chromium, copper, nickel, lead, arsenic and zinc. These heavy metals enter wastewater through several means which include erosion of the soil, natural weathering of the earth's crust, effluents discharge from industries, mining process, sewage discharge and, by the application herbicides to crops (Jaishankar *et al.*, 2014). It's known that heavy metals are hazardous to both human lives and other organisms, their toxic nature can cause low level of energy and also harm to the brain, kidney, liver, blood constituent and hardening of the lungs. Also, exposure to these heavy metals for a long period of time can bring about degeneration of the muscles, physical ability and even the neurons (Jaishankar *et al.*, 2014).

Adsorbents used in the removal of heavy metals from wastewater include TiO$_2$ nanoparticles (as catalyst for aged and complete organic pollutants degradation in ozonation process), zero-valent iron (nanocatalyst used to degrade environmental contaminants), nanostructured ZnO semiconductor films (for organic contaminants degradation) and carbon nanotubes (CNTs).

Carbon nanotube (CNTs) is superior to other adsorbents because of its use in variety of applications. These includes: its use in multiple organics (such as grease, detergent, volatile organic compounds, pesticides, drug molecules and herbicides), inorganic (heavy metals and salt) and in biological (bacteria, fungi, viruses and algae) water pollutants. CNTs possess unique properties such as high strength and elasticity, thermal expansion, high aspect ratio, high surface area, high adsorption capacity and electrical conductivity (Das *et al.*, 2014).

In this study, cobalt-ferrite catalyst supported on kaolin prepared via wet impregnation technique was used for the synthesis of multiwalled carbon nanotubes (MWCNTs). The synthesized CNTs was purified by acid treatment and functionalized with polyethylene glycol. The nanoadsorbents were utilized for the removal of heavy metal (Zinc, Cadmium and Manganese) from pharmaceutical wastewater through the investigation of contact time,

adsorption dosage and temperature. The study also covers adsorption isotherms, kinetic and thermodynamics to describe the mechanism of CNTs.

1. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

2.1.1. Synthesis of Cobalt-ferrites supported on Kaolin

Cobalt-ferrites catalyst was prepared using wet chemical impregnation process with the aid of a kaolin support. 3.64 g of Co $(NO_3)_2.6H_2O$ and 5.05 g of Fe $(NO_3)_3.9H_2O$ were weighed and mixed in a beaker then dissolved in 50 mL of distilled water. 8g of kaolin was added to the solution and the mixture was stirred at 300 rpm, and allowed to age for about 30 minutes. The mixture was oven dried at 140°C for 10 hours. The final obtained mixture was then cooled, grounded and sieved using a 150 micrometer sieve. Calcination was then carried out on the catalyst powders in a furnace at 600°C for a 14 hours to obtained cobalt-ferrites supported on kaolin.

2.1.2. MWCNTS Synthesis

The tubular quartz tube which contains 1.0 g of catalyst was horizontally placed in the CVD furnace. When the CVD machine was switched on, argon flow rate and temperature was initially set to 15 mL/min and 750°C respectively. Once the temperature of machine is heated up to the set temperature, the argon (carrier gas) flow rate will be adjusted to 100 mL/min and acetylene (carbon source) flow rate was opened, and set to 200 mL/min. As the CVD machine reach the pre-set time of 45 minutes, the temperature starts dropping signifying the end of the reaction. At this time, the acetylene flow rate was closed and argon flow rate re-adjusted to 15 mL/min. The automated machine is then allowed to cool to room temperature and the produced CNTs was removed.

2.1.2. Purification of the Synthesis MWCNTS

Acid purification method was used by treating the as-synthesized CNTs with H_2SO_4 and HNO_3 acid with volume ratio 1:3 and sonicated for 90 minutes at 40°C. The mixture was filtered then washed several times until a neutral pH is achieved.

2.1.3. Functionalization of MWCNTs

The purified MWCNTs were functionalized with 20% Polyethylene Glycol (PEG) and 100 ml of 10% Dimethyl formamide (DMF). The mixture was stirred for 18 hours at 25°C. The resulting sample was washed with distilled water and then dried at 105 °C for 8 hr.

2.1.4. Adsorption Process

The influent from pharmaceutical company was collected and stored in an air tight container and kept in freezer. The initial concentrations of the heavy metals were determined before the adsorption process. The effects of the residence time, adsorption dosage as well as the temperature were examined. The Kinetic, isotherm as well as the thermodynamic of the adsorption process were carried out in a batch adsorption process.

2.2. Adsorption Isotherm

2.2.1. The Langmuir Isotherm

The general representation of the linear isotherm model equation is expressed by Equation 1.

$$\frac{1}{qe} = \frac{1}{al}\cdot\frac{1}{Ce} + \frac{kl}{al} \qquad 1$$

The Freudlich isotherm model equation is also expressed as:

$$log\ q_e = log\ k_f + \frac{1}{n}\ log\ c_e \qquad 2$$

Where ce is the equilibrium liquid phase ion concentration in mg/L and qe is the equilibrium solid phase ion concentration also in mg/L.

2. RESULTS AND DISCUSSION

3.1. Material Characterization

The thermal stability of the developed cobalt-ferrites doped kaolin was determined via the TGA technique. The result of the analysis is as depicted in Fig. 1.

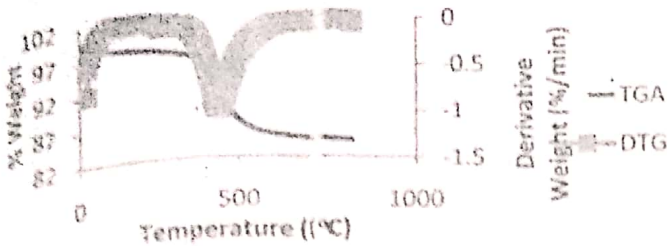

Fig.1 TGA/DTA profile of cobalt-ferrites doped Kaolin

The loss in weight at the temperature range of 30-130°C indicates the loss of water content amounting to about 1.5%. Also, the dehydroxylation of the kaolin takes place at peak temperature of 442°C. The onset temperature of 400°C indicates the stability of the synthesized material to be used for MWCNTs growth at elevated temperature. The SEM images the catallyst after calcination is shown in Fig. 2. Fig. 2 shows the dispersion of solid Fe-Co materials in clusters which are slightly spherical in shape and porous.

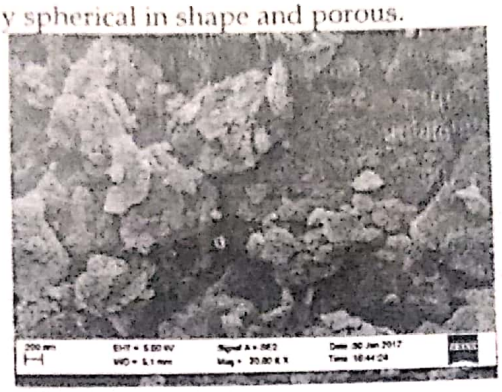

Fig. 2. SEM Micrograph of calcined catalyst

The surface area obtained before calcinations was 345.364 m^2/g, with a pore volume of 0.135 cm^3/g and having a pore size of 3.041nm. This could be attributed to loss of unbound water molecules initially present in the catalyst (Park et al., 2014).

Fig. 3.(a, b, c) show the microstructure of carbon nanotubes for as-synthesized, purified and functionalized respectively. Fig. 3.a showed that CNTs contain catalyst particles that did not partake in the reaction as a result of low carbon source and it is in cluster, while those in Fig.3 (b-c) contains a more refined, clean and elongated CNTs (Abdulkareem et al., 2016) with less metal particles now visibly present on surface of the CNTs i.e. the catalyst particles and support used were removed to a great extent after purification and functionalization (Ravindra and Ramachandra., 2011).

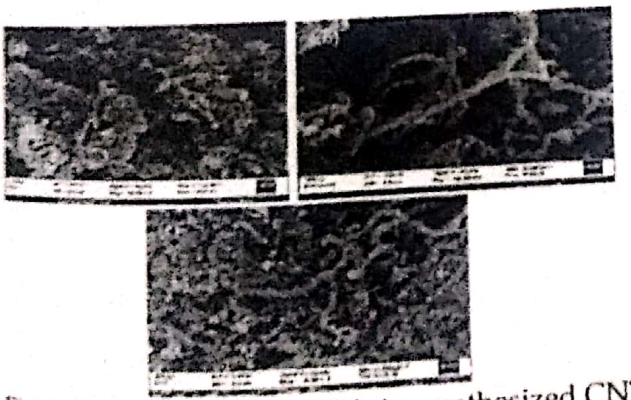

Fig. 3. SEM micrograph of (a) As-synthesized CNTs (b) purified CNTs (c) Functionalized CNTs

Fig. 3. (a, b and c) is the TEM image of the as-synthesized, purified and functionalized CNTs. As shown in Fig. 3, the purified CNTs has enclosed metal particle within the inner diameter of CNTs. TEM image of as-synthesized CNTs has a large clusters of catalyst particles due to aggregation of impurities in form of metals. This is shown by the dark spot present on the image. Whereas, the functionalized CNT present in Fig. 3c has less impurities and forms a medium to high crystallinity CNTs. The internal and external diameter is 21.6 and 43.6nm respectively.

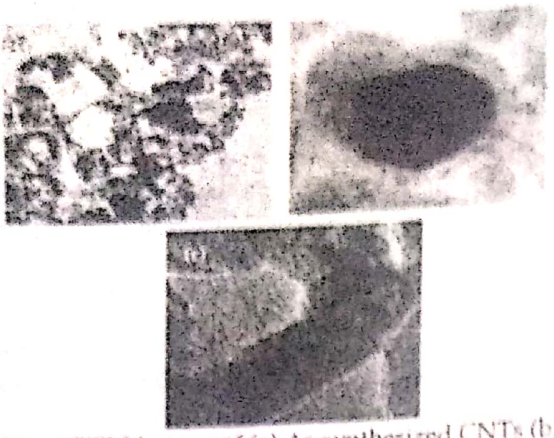

Fig. 4. TEM images of (a) As-synthesized CNTs (b) Purified CNTs (c) Functionalized CNTs

3.2. Adsorption Process

The effects of the adsorbent dosage, residence time and temperature were examined on the percentage adsorption on Zn, Cd and Mn.

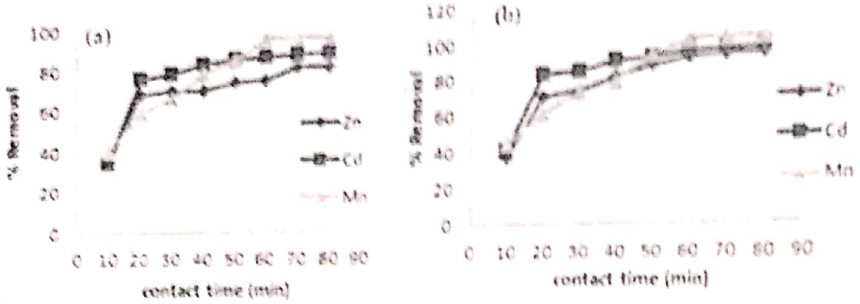

Fig. 5. Plot of %removal against contact time for (a) purified CNTs. (b) functionalized CNTs.

The percentage removal of Zn, Cd and Mn are 80%, 86.7% and 95% respectively. Before it got to the contact time of 60 minutes, the initial adsorption in Fig. 5a rate was very quick and then slows down afterwards. This could be attributed to availability of active sites on surface of CNTs. Afterwards; the adsorption becomes slow until saturation is attained. Equilibrium time in this case is 60 minutes which was where the optimum removal for ZN, Cd and Mn occurred. No significant adsorption was observed after 60 minutes of contact time. Therefore, 60 minutes was considered as optimum for the adsorption process. The increase in the adsorption capacity of the functional CNTs is as a result of its appreciated surface area.

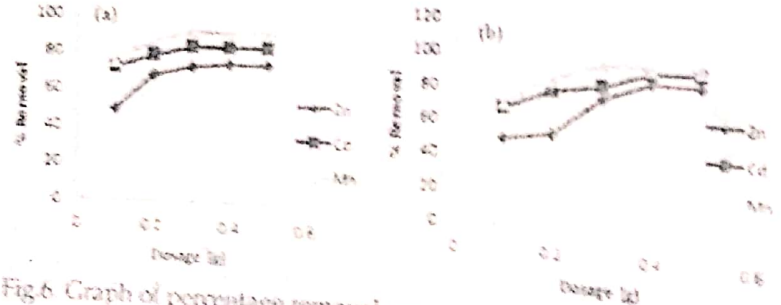

Fig.6. Graph of percentage removal against adsorbent dosage for (a) purified CNTs (b) functionalized CNTs

The effect of adsorption dosage on adsorption rate of purified and functionalized MWCNTs was carried out and the results obtained are shown in Fig. 6 (a-b). The graph shows that as adsorbent dosage was increased, the percentage removal of Zn, Cd and Mn obtained were 72.15%, 82.26% and 90.28% respectively. With the increase in dosage to 0.5g, there wasn't any significant increase in percentage removal of the metals. This is in accordance with the report of Sari et al. (2007) and Huang et al. (2014).

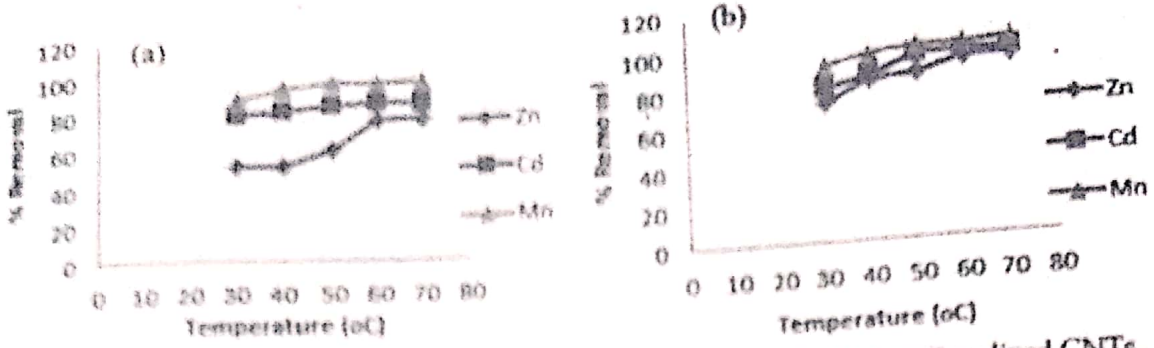

Fig 7 Graph of % removal against temperature for (a) purified CNTs (b) functionalized CNTs.

Fig. 7 shows that as the temperature was increased from 30 – 70°C, there was a corresponding increase in the percentage removal and the equilibrium temperature attained for Zn was 60 °C. There was no significant change in the rate of adsorption by the purified CNTs for Cd (79.42% at 30 °C till it got to 84.06% at 70 °C) and Mn (93.75% at 40 °C slight rise to 95.25% at 70 °C) in respect to the equilibrium temperature. The decreased adsorption after the equilibrium temperature is as a result of reduced surface activity at higher temperatures.

3.3. Adsorption Isotherm.

Adsorption isotherm is usually applied to analyze experimental data at equilibrium. In this study, Langmuir and Freundlich model were used to analyze the adsorption data. It was reported that model with R^2 value closer to unity is the most appropriate for adsorption process. The result of the isotherm model is presented in Table 1.

Table 1. Isotherm parameters for adsorption of heavy metal ions on purified and functionalized CNTs.

Metals	Purified CNTs			Functionalized CNTs		
	Q_m		K_l	Q_m		K_l
	R^2			R^2		
Langmuir Adsorption Isotherm parameters						
Zn	0.040 05	351.69 01	0.652 0	0.13 [illegible]03	- 19.63 42	0.9 98
Cd	0.042 43	57.76[illegible] 6	[illegible]	[illegible] 063	174.5 989	0.7 41
Mn	0.193 24	-1.7279	0.896	0.14 188	16.66 17	0.9 13
Freudlich Adsorption isotherm parameters						
Metals	Purified CNTs			Functionalized CNTs		
	N		K_f	n		K_f
	R^2			R^2		
Zn	2.557 5	0.1702	0.843	0.75 24	15.41 7	0.9 93
Cd	1.545 6	0.2938	0.707 2	2.45 10	0.117 8	0.7 34
Mn	0.805 2	0.7211	0.932	2.11 86	0.252 3	0.9 59

Table 1 shows the constants and correlation co-efficient of Langmuir and Freundlich model. As shown in Table 1, Cd has n < 1, which implies that P-CNTs is favourable for adsorption of Cd. However, F-CNT is favourable for adsorption of Cd and Mn. However, when comparing the two isotherm models, adsorption data is best fitted to Freundlich isotherm.

3.4. Adsorption Kinetic

In this study, adsorption kinetics of purified and functionalized CNTs were done with pseudo-first order and pseudo second order kinetics models to show time effect on the adsorption capacity of Zn, Cd and Mn on P-CNTs and F-CNTs. The constants and their correlation coefficient are shown in Table 2.

Table 2. Kinetic parameters of heavy metal ions on purified and functionalized CNTs.

	Purified CNTs			Functionalized CNTs		
Kinetic Parameters	Zn	Cd	Mn	Zn	Cd	Mn
Pseudo first order						
K1 (min-1)	0.08291	0.0898	0.0415	0.0622	0.0668	0.0461
Qe	0.5984	0.631	1.7219	0.8511	0.4198	2.4547
R^2	0.85	0.878	0.798	0.953	0.96	0.98
Pseudo Second order						
K2 (min-1)	0.0994	0.1272	0.0197	0.0635	0.1219	0.0126
Qe	0.8718	0.6510	2.6954	1.0395	0.7042	2.9940
R^2	0.987	0.973	0.994	0.988	0.985	0.951

According to Table 2, the correlation co-efficient of Pseudo second order kinetic model for P-CNTs and F-CNTs was found to be higher than Pseudo first order kinetic model. Thus, adsorption of Zn, Cd and Mn are best described to Pseudo second order kinetic model.

3.4. Thermodynamics Studies

The thermodynamic study was carried out to enable the determination of Gibbs free energy (ΔG), entropy (ΔS) and enthalpy (ΔH) of the adsorption process. The results of the thermodynamics studies is as depicted in Table 3. As shown in Table 3 the Gibbs free energy values obtained for the adsorption process for the temperature interval of 303K to 343K for the adsorption of Zn are -1546.2, -2166.6, -2787.0, -3407.4 and -4027.8(Kjmol^{-1}) respectively. For the adsorption of Cd, the values obtained were - 3729.9, -4606.2, -5482.5, -6358.8 and -7235.1(Kjmol^{-1}) respectively and -5113.1, -7274.7, -9436.4, -11598.0 and -13759.7(Kjmol^{-1}) respectively for Mn. The negative free energy change (ΔG) values for Zn, Cd and Mn indicates the spontaneous nature of adsorption process of the purified and also the functionalized CNTs over the studied range of temperature

Table 3. Thermodynamics parameters of heavy metals adsorption on Purified and Functionalized CNTs

Adsorbate	Temp (K)	ΔH (kJmol-1)	ΔS (J/K.mol)	ΔG (kJmol^{-1})	Adsorbent
Zn	303	17251.6	62.0391	-1546.2	P-CNTs
	313			-2166.6	
	323				

				2787.0	
	333			-3407.4	
	343			-4027.8	
Cd	303	22821.9	87.629	-3729.9	P-CNTs
	313			-4606.2	
	323			-5482.5	
	333			-6358.8	
	343			-7235.1	
Mn	303	60384.6	216.164	-5113.1	P-CNTs
	313			-7274.7	
	323			-9436.4	
	333			-11598.0	
	343			-13759,7	
Zn	303	48728.4	171.601	-3266.7	F-CNTs
	313			-4982.7	
	323			-6698.7	
	333			-8414.7	
	343			-10130,7	
Cd	303	33921.1	123.213	-3412.5	F-CNTs

	333			0	
	343			3407.4 - 4027.8	
Cd	303	22821.9	87.629	- 3729.9	P-CNTs
	313			4606.2 - 5482.5	
	323			6358.8 - 7235.1	
	333			- 5113.1 - 7274.7	
Mn	303	60384.6	216.164	- 9436.4 - 11598.0	P-CNTs
	313			- 13759.7	
	323			- 3266.7 - 4982.7	
	333			- 6698.7 - 8414.7	
	343			- 10130.7	
Zn	303	48728.4	171.601	- 3412.5	F-CNTs
	313				
	323				
	333				
	343				
Cd	303	33921.1	123.213		F-CNTs

	313			-4644.7	
	323			-5876.8	
	333			-7108.9	
	343			-8341.1	
Mn	303	40913.2	155.472	-6194.8	
	313			-7749.5	F-CNTs
	323			-9304.3	
	333			-10858.9	
	343			-12413.7	

CONCLUSIONS

The adsorption efficiency of purified and functionalized CNTs for the removal of Zn, Cd and Mn from pharmaceutical wastewater were investigated in this study. The catalyst was prepared by wet impregnation method. The catalyst yield obtained was 93.21 % at a temperature of 140 °C, drying time of 10 hours, stirring speed of 500 rpm and a mass of 8g. The CNTs was synthesized in a CVD reactor by a decomposition of acetylene in the presence of bimetallic Fe-Co/kaolin catalyst at 100 mL/min argon flow rate, 200 mL/min acetylene flow rate, 750 oC reaction temperature, and 45 minutes reaction time. The synthesized CNTs obtained were purified by acid treatment and functionalized with PEG. TEM analysis revealed that F-CNTs was crystalline in nature. BET results revealed that F-CNTs had an improved surface area of 970.81 m2/g than P-CNTs. The nano-adsorbents were employed for the adsorption of selected heavy metals and other contaminants from pharmaceutical wastewater. Optimum adsorption was obtained at adsorbent dose of 0.4 g, 60 °C and equilibrium time for adsorption was achieved within 60 min of contact time with percentage removal of 89.78, 94.65 and 93.32 % for Zn, Cd and Mn respectively on to F-CNTs. The increase in surface area of the nano-adsorbents contributed to its effectiveness in adsorption process. The kinetic studies of pharmaceutical wastewater were fitted to the pseudo-second order kinetics and Freundlich model described the adsorption isotherm. The thermodynamics data revealed that ΔG was negative which implies spontaneity of adsorption process. The values of ΔH were all positive illustrating endothermic nature. The values of ΔS obtained were positive indicating an increase in the disorderliness of the system. Finally, a decrease in physicochemical properties of pharmaceutical wastewater was observed due to effectiveness of nano-adsorbents.

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