Diclofenac sodium removal from water samples using chitosan nanocomposites modified with multi-walled carbon nanotubes

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This study explores the preparation of chitosan blended with MWCNTs as an adsorptive material for DCF sodium from water samples. Synthesised chitosan nanocomposites were characterised using FTIR, XRD, SEM and BET analysis. The optimal conditions to improve DCF sodium removal to 98% were at pH of 3, adsorbent dosage of 2.5 g/L, 30 minutes contact time and 20 mg/L initial concentration. Kinetic studies exhibited that DCF sodium adsorption fitted pseudo second order ($R^2 = 0.997$) and the isotherms best fitted the Freundlich isotherm model ($R^2 = 0.997$). The 3% MWCNTs-Chitosan nanocomposite could be reused at least 5 times indicating a significant effectiveness of this adsorbent for DCF sodium pharmaceuticals removal.

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1. Introduction

One of the global environmental issues that need more attention and improvement is water quality. The availability of potable water for domestic use remains a major concern in both developed and developing countries [1]. An increase in the scarcity of clean drinking water is one of the most serious environmental challenges experienced in many parts around the world. Considering the rate of population growth, the amount of freshwater available is expected to decline with time and this will negatively affect socio-economic development in many countries [2]. Pharmaceuticals are persistent water contaminants that have low degradability and are highly toxic. The occurrence of pharmaceuticals in drinking water even at minimal acceptable concentration levels, have negative effects on human health [3]. It has been reported that pharmaceutical residuals widely spread in different water sources including portable water, ground water and municipal wastewater [4,5]. Introduction of harmful pharmaceutical substances in these water sources contribute greatly to water pollution which also increases water shortage in the process [6].

Diclofenac (DCF) sodium is a pharmaceutical drug which is broadly utilised for the treatment of aching and inflammatory conditions by humans due its non-steroidal and antiinflammatory properties [7]. After consumption for treatment purposes, DCF sodium is commonly metabolised to its methoxylated and hydroxylated derivatives, excreted usually in urine in their glucuronide-conjugated and free forms [8]. Sewage treatment plants are usually unable of removing DCF sodium in high percentages, which results later in their presence in potable, surface and groundwater water samples [9]. Drinking water polluted with DCF sodium might cause gastrointestinal damage, platelet dysfunction cytotoxicity of liver, kidney and convolution for humans [9,10]. Since the elimination efficacy of DCF sodium is little in water treatment plants, numerous approaches such as ozonation, photocatalysis and anodic oxidation have been explored [11–14]. However, these techniques result in the creation of residual poisonous by-products adding to great treatment amount [15]. It will then be vital to investigate more effective and affordable methods of DCF sodium elimination from polluted water samples. Adsorption is considered as a preferential alternative method because it has been shown to can eradicate pollutants and

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successfully prevent the production of several poisonous intermediates [16]. Various materials including graphene oxide, multi-walled carbon nanotubes, activated carbon, metal organic frameworks and activated sludge, were reported to efficiently adsorb DCF sodium due to their abundant adsorption sites and high specific surface area [7,17–19]. However, nanomaterials suffer some disadvantages, such as poor recovery ability, agglomeration and difficult separation, which interferes with practical applications in real water [20].

Chitosan is a natural polymer and a product of alkaline deacetylation process of chitin. It is affordable and more efficient compared with activate carbon and other conventional adsorbents utilised in wastewater treatment [4,21]. The biopolymer chitosan has been chosen in this study due to its non-toxicity, biodegradability, effective moldability, hydrophilic nature and its environmentally friendliness [22,23]. Pure and modified chitosan can be regarded as a capable adsorbing material which can be utilised for treatment of toxic water contaminants due to its ability of chelation with poisonous pollutants such as heavy metals, dyes and pharmaceuticals [21]. Recent studies conducted on the possibility of modifying chitosan with various functional groups which will affect the physicochemical parameters of the attained derivatives include N-acyl modifications, N-alkyl modifications, quaternization and C-6 oxidation [24]. Chitosan can be modified with functional materials such as multi-walled carbon nanotubes (MWCNTs) to form a nanocomposite material through graft modification or crosslinking to enhance its adsorption capacity towards contaminants in water samples. This can be achieved by crosslinking, co-precipitation methods, or electrochemical methods on the surface of chitosan [24]. Modification of polymers such as chitosan through the crosslinking method has shown better removal of pharmaceuticals acidic media compared to the unmodified chitosan. Crosslinking can be achieved either through a physical or chemical method depending on the type of relations between chitosan and the agents used for crosslinking [25]. Modification of chitosan using crosslinking agents also makes it highly stable because of the formed covalent bonds [26].

Applications of MWCNTs have mainly focused on their usage in composites as an additive in a variety of medical, heavy metal removal and biotechnological applications. This is because of their high biocompatibility and their high ability to attach specific proteins to functional groups [21,27]. Previously, the modification of MWCNTs on Poly(Vinylidene Fluoride-Co-Hexafluoropropene exhibited great results on adsorption of heavy metal because of their remarkably high adsorptive capacity [28]. In this study, we combine chitosan and MWCNTs for adsorption of DCF sodium from water samples. The introduction of MWCNTs on chitosan will assist by providing more binding sites and may also enhance the surface area which will improve the adsorption capacity of the nanocomposites [29]. The synergy between chitosan and MWCNTs enhances the stability and electrical conductivity of the nanocomposite, while chitosan behave as a durable matrix for MWCNTs dispersal [29]. Herein, the study present an efficient approach for the adsorption of DCF sodium pharmaceutical from water samples showing distinct benefits, such as increased adsorption capacity and reusability of prepared nanocomposites.

2. Materials and methodology

2.1. Materials

Analytical grade reagents used in this research such as chitosan, multi-walled carbon nanotubes (MWCNTs), sodium diclofenac, sodium hydroxide (NaOH), glutaraldehyde, nitric acid (HNO₃) and sulfuric acid (H₂SO₄) were all purchased from Merck Life Science (Pty) Ltd, Johannesburg, South Africa.

2.2. Preparation of chitosan beads

To prepare chitosan composite, chitosan (2g) was dissolved in acetic acid solution (90 mL, 5%). The solution was left overnight stirring before it was added dropwise into a beaker containing 500 mL of NaOH (0.50 M) while stirring to form chitosan beads. The resultant chitosan beads were filtered and washed with ultrapure water. The beads formed were then left in a solution of 0.026 M solution of glutaraldehyde (120 mL) for 24 hours at room temperature before they were washed with

ultrapure water and dried in the oven at 40 °C. The process was followed by crushing the beads in to power after drying.

2.3. Preparation of MWCNTs chitosan nanocomposite

To prepare MWCNTs-Chitosan nanocomposite, chitosan (2 g) was dissolved in acetic acid solution (110 mL, 5%) in a 250 mL beaker. Separately, MWCNTs (0.02 g) functionalised using 1:3 HNO₃/H₂SO₄ acids were added into 30 mL of acetic acid (5%) and sonicated for 30 minutes [30]. The two solutions were then combined and left overnight while stirring before dropwise addition into a beaker consist of 500 mL NaOH (0.50 M). The resultant chitosan beads were filtered and washed with ultrapure water. The newly formed 1% MWCNTs-chitosan beads were left standing for 24 hours in 0.026 M solution of glutaraldehyde (120 mL) solution at room temperature after which they were filtered, washed with ultrapure water and dried in the oven at 40 °C. This was followed by crushing the beads in to power after drying. 2% MWCNTs-chitosan and 3% MWCNTs-chitosan composites were prepared the same way while using 0.04 g and 0.06 g of functionalised MWCNTs respectively.

2.4. Characterisation

The morphology of the chitosan nanocomposites was analysed utilising a Auriga Zeiss-39-42 scanning electron microscope with Germini FE-SEM column. The Micromeritics 2020 Brunauer Emmett Teller (BET) instrument was used for surface studies analysis, while an Agilent Cary 600 series FTIR spectrophotometer was utilised for functional groups analysis (500 to 4000 cm⁻¹ wavelength). The crystallinity analysis using X-Ray diffractometer was done on a Philips X-Ray Diffractometer PW 1830 in a 2-theta ranging from 5 to 80 degrees with Cu Ka ($\lambda = 0.154$ nm).

2.5. Batch adsorption studies

The calibration standards with the concentration range of 10 to 50 mg/L DCF sodium at a wavelength of 275 nm were prepared from a DCF sodium stock solution (200 mg/L). Various parameters which influence the process of adsorption were studied in batch adsorption studies. This included adsorbent dosage (from 0.5 to 2.5 g/L), pH of the solution (ranging from 1 to 11), interaction time (ranging from 5 to 30 min), and initial DCF sodium concentration (ranging from 10 to 100 mg/L). The pH was adjusted by using both NaOH and HNO₃ at a concentration of 0.1 M. All the experimental runs were done at room temperature (25 °C) while starring at 300 rpm speed for all conditions. After adsorption experiments, UV-Vis spectrophotometer was utilised for analysing the concentration of DCF sodium in water samples. The percentage removal and the amount of DCF sodium pharmaceutical adsorbed (mg/g) was determined using the following equations [29,31]:

% removal =
$$\frac{(C_o - C_e)}{C_o} \times 100$$

 $q_e = \frac{(C_o - C_e)V}{m}$

wherein C_o is for DCF sodium (mg/L) initial concentration, Ce is for equilibrium concentration of the DCF sodium adsorbed (mg/L), qe stands for the adsorption equilibrium (mg/g), V is volume of the solution (L) while m is the adsorbent mass (g).

3. Results and discussion

3.1. Characterisation

The FTIR spectra of Chitosan and MWCNTs-chitosan nanocomposite is presented in Fig. 1. The characteristic peaks of chitosan (Fig. 1b) noted at 789 and 1076 are attributed to C–O in the anhydroglucose ring, while the 1357 and 1660 are attributed to N-acetylglucosamine and bending vibration of N-H in the amide group of the chitosan molecule, confirming the presence of chitosan. The 3290 cm⁻¹ broad peak (Fig. 1a) is depicted to the widening vibration of O-H conforming the presence of MWCNTs on the chitosan composite as reported in literature [29].



Fig. 1. FTIR spectra of (a) MWCNTs-chitosan nanocomposite and (b) Chitosan.



Fig. 2. XRD patterns of (a) MWCNTs, (b) chitosan, (c) 1% MWCNTs-chitosan, (d) 2% MWCNTs-chitosan and (e) 3% MWCNTs-chitosan.

Fig. 2 shows the X-ray diffraction patterns of functionalised MWCNTs, Chitosan, 1% MWCNTs-chitosan, 2% MWCNTs-chitosan and 3% MWCNTs-chitosan. The characteristic diffraction peak of MWCNTs (Fig. 2a) was approximately 26.4° corresponding to the hexagonal graphitic support structure. The diffraction peak of chitosan (Fig. 2b) was approximately at 2θ values of 20° indicating the amorphous chitosan state. For the MWCNTs-Chitosan pattern (Fig. 2c to e), the dominant peak at 2 theta = 26.4° a characteristic of MWCNTs, was still slightly intense, demonstrating good crystallinity of 3% MWCNTs-Chitosan nanocomposite as reported in literature [32]. In addition, increasing the concentration of MWCNTs (Fig. 2c to e) did not show any significantly enhanced peak, since only a small percentage of MWCNTs was introduced as noted in literature [33].



Fig. 3. SEM images of (a) Chitosan and (b) MWCNTs-Chitosan nanocomposites.

Fig. 3 shows the SEM images of Chitosan and MWCNTs-chitosan nanocomposites. SEM images of the nanocomposites displayed loosely bound grains shaped molecules with random and rough surfaces with sizes ranging between 2 and 12 μ m as reported in literature [26]. After modification of Chitosan by MWCNTs, visible nanotubes confirming the presence of MWCNTs were noted, intertwined with the chitosan composites, and the chitosan surface structure was more intact compared to that of the chitosan alone.

Samples	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
MWCNTs	234.9	1.756
Chitosan	1.1502	0.000290
1% MWCNTs-Chitosan	1.1952	0.000391
2% MWCNTs-Chitosan	1.2887	0.000578
3% MWCNTs-Chitosan	1.9082	0.000784

Table 1. BET surface analysis of MWCNTs, Chitosan and MWCNTs-Chitosan nanocomposites.

The surface area and pore volume of MWCNTs, Chitosan, 1% MWCNTs-Chitosan, 2% MWCNTs-Chitosan and 3% MWCNTs-Chitosan are recorded in Table 1. BET surface area analysis was undertaken to determine the surface area, which may correspond to the adsorption efficiency of the nanocomposites. The process of blending chitosan onto MWCNTs resulted in the homogeneous dispersion of MWCNTs of the chitosan polymer matrix. It was noted that when MWCNTs was introduced to chitosan, there was a slight improvement on the pore volume and surface area as the percentage of MWCNTs was increased, similar to the work reported elsewhere [34].

3.2. Effect of adsorbent dosage

The adsorbent dosage effect of chitosan nanocomposites on the removal of DCF sodium is shown in Fig. 4. The study was done at adsorption dosage range of 0.5 to 2.5 g/L for 60 minutes. The results show an increase in adsorption percentage when the concentration of chitosan nanocomposites was increased. The 3% MWCNTs-Chitosan composite gave the highest percentage adsorption of 91% on the 2.5 g/L adsorbent dosage. This is because when the adsorbent dosage was increased, the adsorption sites of the nanocomposites were also enhanced, hence it increased the amount of DCF sodium removal [35].



Fig. 4. Adsorbent dosage effect on the removal of DCF sodium from water samples.

3.3. Effect of pH

The pH effect during the adsorption of DCF sodium using Chitosan and 1,2,3 % of MWCNTs-Chitosan nanocomposites is reported in Fig. 5. The study was done at a pH range 1 to 11 for 60 minutes at an adsorbent dosage of 2.5 mg/L. The results indicated that, between pH of 1 and 3 there was a slight increase in adsorption percentage which then reduced with when pH was increased from 3 to 11. Hence the highest DCF sodium adsorption was reported at pH of 3 for all the chitosan nanocomposites with the 3% MWCNTs-Chitosan composite giving the highest percentage adsorption of 90%. The results indicated better adsorption in acidic solution than in alkaline solution at pH of 3 which is less than the pKa of DCF sodium (pKa = 4.20). This is because DCF sodium occurs in its neutral form, with a decreased solubility when in water; hence as the pH is increased, the 'van der Waal' interface among DCF sodium pharmaceutical and the nanocomposite decreases by physical adsorption [9,35].



Fig. 5. The pH effect on the removal of DCF sodium from water samples.

3.4. Effect of time

The effect of time during the adsorption of DCF sodium using Chitosan and 1,2,3 % of MWCNTs-Chitosan nanocomposites is shown in Fig. 6. This was done in the range of 5-120 minutes, 2.5 g/L adsorbent dosage and pH of 3. The findings showed that adsorbed amount of DCF sodium chitosan nanocomposites increased as the contact time was increased for all the nanocomposite membranes. The DCF sodium adsorption attained equilibrium slightly in about 15

minutes for all the nanocomposites, which then increased after 30 minutes reaching the final equilibrium after 30 minutes, the 3% MWCNTs-Chitosan nanocomposite gave the highest adsorption of 95%. This indicated that between 15 and 30 minutes, there was no significant adsorption as the difference was noted after 30 minutes and consequently reaching equilibrium at 30 minutes. This has shown improved results when compared to the study reported in literature wherein equilibrium was reached after 100 min with a percentage removal of around 70% [35].



Fig. 6. Time effect on the removal of DCF sodium from water samples.

3.5. Effect of initial concentration

The concentration effect during the adsorption of DCF sodium using Chitosan and 1,2,3 % of MWCNTs-Chitosan nanocomposites is shown in Fig. 7. The influence of concentration was investigated (20 to 100 mg/L) at a dosage of 2.5 g/L, pH of 3 and contact time of 30 minutes. The results displayed that as the concentration of 2.5 g/L adsorbent dosage and pH of 3n increased, percentage removal of DCF sodium decreased for all the chitosan nanocomposite membranes with 3% MWCNTs-Chitosan nanocomposite showing the highest percentages from 98 to 59%. This implies that at higher concentrations, the active sites on the nanocomposite adsorbent surface got saturated by the DCF sodium due to a shortage of the active sites on the chitosan nanocomposites. Similar findings were reported in literature [36] during the adsorption of reactive blue 19 (RB19) on magnetic graphene oxide/chitosan nanocomposite beads.



Fig. 7. Initial concentration effect on the removal of DCF sodium from water samples.

3.6. Adsorption kinetics

The adsorption kinetics of DCF sodium by the 2% and 3% MWCNTs-Chitosan nanocomposite was studied using the pseudo first order and second order kinetics models as shown in the equations below:

In
$$(q_e - q_t) = Inq_e - k_1 t$$
 pseudo first order
 $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$ pseudo second order

wherein, $q_t (mg/g)$ represents the DCF sodium absorbed at time (t), while $q_e (mg/g)$ is the adsorbent amount at equilibrium. $k_1 (min^{-1})$ is the pseudo first order kinetic constant (min^{-1}) and k_2 is the pseudo second order rate constant of sorption (g/mg·min). The values for k and q_e of DCF sodium were derived from the intercept and slope, respectively, and are detailed in Table 2.



Fig. 8. (a) Pseudo first order and (b) pseudo second order kinetic models.

The kinetic models capable of describing DCF sodium adsorption are shown in Fig. 8 and table 2. The results revealed that the pseudo first order model was inefficient for defining DCF sodium adsorption kinetics. The pseudo second order model exhibited high correlation coefficients of 0.9752 and 0.9973 for the 2% MWCNTs-Chitosan nanocomposite and 3% MWCNTs-Chitosan nanocomposite, respectively. The pseudo second order model assumes chemisorption which could be a remarkable mechanism for DCF sodium adsorption by chitosan nanocomposites as noted in literature [37].

Table 2. Calcu	lated kineti	c model.

Material	$q_e(exp)$	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	(mg/g)	K_1 (min ⁻¹)	$q_e (mg/g)$	R ²	K ₂	$q_e (mg/g)$	R ²
					(g/mg.min)		
2% MWCNTs-Chitosan	7.165	0.0004	6.943	0.777	0.0555	4.699	0.975
3% MWCNTs-Chitosan	7.591	0.0005	6.527	0.944	0.0559	11,14	0.997

3.7. Adsorption isotherms

Freundlich and Langmuir adsorption isotherm models were studied to understand the DCF sodium adsorption process between the chitosan nanocomposites and DCF sodium ions. Langmuir model describes the monolayer adsorption occurring on the surface with adsorption taking place at

fixed number of adsorption sites with no lateral interaction. The following equation shows the linearised Langmuir isotherm model equation [29]:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e}$$

 C_e is the concentration of DCF sodium (mg/L), K_L stands for the Langmuir constant (L/mg), q_{max} is the maximum adsorption capacity (mg/g) and q_e is the amount of DCF sodium absorbed per gram of the adsorbent (mg/g), R_L , is the Langmuir separation factor which is a dimensionless constant is calculated by the following formula:

$$R_L = \frac{1}{1 + bC_o}$$

where $R_L = 0$ suggests irreversibility of the adsorption process, $R_L > 1$ represents unfavourable adsorption, $R_L = 1$ indicates linear adsorption isotherm, while $0 < R_L < 1$ signifies favourable adsorption.

The Freundlich isotherm model on the other hand suggests an empirical model which characterises adsorption on heterogeneous surfaces through non-uniform distribution and multilayer adsorption. It is given by the following formula:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

where 1/n (dimensionless) and K_F (mg^{1-1/n} L^{1/n} g⁻¹) are the Freundlich constants linked with the adsorption intensity and adsorption capacity respectively.



Fig. 9. (a) Langmuir isotherm and (b) Freundlich isotherm.

Material	q _{max} (mg/g)	Langmuir kinetic model			Freundlich kinetic model		
		b (L/mg)	R _L	R ²	K_{f} (mg/g)	n	\mathbb{R}^2
2% MWCNTs-Chitosan	21.053	0.0283	0.638	0.971	5.298	1.908	0.992
3% MWCNTs-Chitosan	23.53	1.28	0.0424	0.983	6.495	2.353	0.996

Table 3. Langmuir and Freundlich isotherm parameters.

Fig. 9 shows the linearised data obtained using Langmuir and Freundlich isotherm of DCF sodium on 2% MWCNTs-Chitosan nanocomposite and 3% MWCNTs-Chitosan nanocomposite. The isotherm parameters are recorded in table 3. The obtained data imply that the processes of adsorption by chitosan nanocomposites is well conformed the Freundlich ($R^2 = 0.996$) model (Fig. 9 and table 3) looking on the R^2 values. As such, the Freundlich adsorption isotherm model suggests that DCF sodium was adsorbed by initially inhabiting the stronger binding sites of the adsorbent with subsequent exponential decay in the adsorption energy occurring at the end of the adsorption process. In table 3, the (n) values were greater than one, indicating favourable adsorption between DCF sodium adsorbate and the chitosan nanocomposite adsorbent surface was accomplished.

3.6. Reusability studies

Fig. 10 show the reusability of the 3% MWCNTs-Chitosan nanocomposite for DCF sodium adsorption. After performing adsorption tests, the nanocomposites were regenerated by using 0.1 M NaOH to assess their reusability. The nanocomposites were soaked in 0.1 mol/L NaOH solution for 10 minutes, then rinsed with deionised water and dried before being reused at least 5 times. The first removal efficiency of 3% MWCNTs-Chitosan nanocomposites was 98.54%, and after five successive cycles the adsorption reduced to 92.08% with an adsorption loss of only 6.5%. The results indicate that after five cycles the removal efficiency of the 3% MWCNTs-Chitosan remained stable although it slightly reduced. The good reusability of the 3% MWCNTs-Chitosan nanocomposites is probably due to their higher mechanical strength and the availability of more functional groups (MWCNTs) after the regeneration process [4,32].



Fig. 10. Reusability of the 3% MWCNTs-Chitosan nanocomposite for DCF sodium adsorption.

4. Conclusion

Chitosan and Chitosan-MWCNTs nanocomposites were synthesised and utilised during the adsorption of DCF sodium pharmaceuticals from water samples. Characterisation of the prepared chitosan nanocomposites analysed by FTIR, SEM and XRD corroborated the presence of MWCNTs on chitosan, the morphology of the modified chitosan and the crystallinity of the chitosan nanocomposites respectively. BET analysis showed an improvement of the surface area when the percentage of MWCNTS was increased. The removal efficiency of DCF sodium using chitosan and chitosan modified with MWCNTs was examined in batch studies studying the influence of pH, adsorbent dosage, time and initial concentration.

The 3% MWCNTs-Chitosan nanocomposite reached a maximum removal of 98% at optimised conditions which indicated that chitosan nanocomposites synthesised were effective in removing DCF sodium from water samples. The optimal conditions obtained from the DCF sodium adsorption were at pH 3, 2.5 g/L adsorbent dosage, 20 mg/L concentration and 30 minutes contact time.

The kinetic data fitted the pseudo-second order kinetic model ($R^2=0.9973$) and the isotherm studies followed the Freundlich isotherm model ($R^2 = 0.996$), suggesting multilayer heterogenous adsorption on a multilayer surface. The 3% MWCNTs-Chitosan nanocomposite could be well regenerated in 5 cycles with an adsorption loss of 6.5%. The results indicate that 3% MWCNTs-Chitosan nanocomposite is a good candidate for DCF sodium pharmaceutical adsorption in wastewater.

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