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Remediation of polluted water by diclofenac drug by adsorption technology

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ABSTRACT/RESUME

Abstract:*. In this paper, we addressed the issue of using organo-K10 montmorillonite as adsorbent of DS to remove it from aqueous environment. An organo-K10 montmorillonite (MK10-C16) was prepared by intercalating the organic cation cetyltrimethylammonium bromide (C16) in a K10 montmorillonite (MK10), than characterized using XRD analytical technique. The organo-K10 montmorillonite displayed enhanced affinity for the DS in water. Using a linear regression, the pseudo-second-order model describes better the results of the kinetics. The adsorption data fitted well with Langmuir isotherm. The maximum adsorption capacity of diclofenac is estimated to be 63.33 mgg^{-1}. The results revealed that MK10-C16 have a high potential to be used as adsorbent for the removal of DS from aqueous solution.*

I. Introduction

Drugs are designed to affect biochemical and physiological functions of biological systems, their presence in water environment means that they may elicit biochemical and physiological changes in aquatic organisms. Diclofenac, an acidic pharmaceutical compound which belongs to the non-steroidal anti-inflammatory drugs (NSAIDs) family, is one of the compounds most commonly found in aquatic environments, its overall yearly worldwide consumption as a human and veterinary pharmaceutical drug is more than 1000 tons/year [1]. Diclofenac has a low solubility, high log K_{ow} value, low dipole moments and negative charges, which causes its easy escape from the nano-filtration units [2]. This drug causes the population decline of Asian vultures after consuming carcasses of Diclofenac-treated cattle, resulting in irreversible damage to their kidneys [3-5] and histopathological effects in trout species at relatively low concentrations around 1.0 to 5.0 µg/L [6-9]. Adsorption, which is fully dependent on the development of new adsorbents, is one of the removal technological promising approach. The research of natural or modified natural adsorbents is a strategy to remediate contaminated water produced by humain activities. In addition, application of environmentally friendly adsorbents into natural systems is particularly important to entail minimal environmental impact.

Objectives of the present study were:

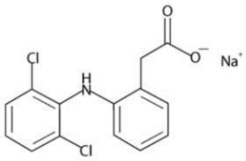
- The preparation and characterization of an organo modified K10 montmorillonite, consisting of K10 montmorillonite intercalated with cetyltrimethylammonium bromide cations.
- Its application in the removal of Diclofenac sodium from water under several experimental conditions.

II. Materials and methods

II.1. Adsorbent Preparation

K10 montmorillonite (MK10), Cetyltrimethylammonium bromide (C16) and diclofenac sodium (Table 1 provides the structural and chemical properties of diclofenac) were supplied by Sigma–Aldrich. The organo-K10 montmorillonite was obtained by cation exchange by C16 in an acidic medium according to Tiwari et al. [10]. Obtained adsorbent was characterizd by Xray diffraction using Bruker Advanced X-ray machine. The Cu Kα radiations having wavelength of 1.5418 Å.

***Table 1.** The structural and chemical properties of Diclofenac.*

Molecular formula	Structural formula	Molecular weight (g mol^{-1})	log K_{ow}	Dipole moment (Debye)
$C_{14}H_{10}Cl_2NNaO_2$		318.13	4.51 [2]	0.966 [2]

II.2. Batch Adsorption Experiments

Batch experiments were performed with 50 mL of DS solutions of predetermined initial concentration (5-500 mgL^{-1}) in flasks. 50 mg of adsorbent were added to each flask, and the solution was agitated at 295 K for 2 hours. After that, the DS solutions were centrifuged, filtated and the filtrates were subjected to the bulk concentration of diclofenac at λ_{max} = 267 nm.

Time dependence adsorption of diclofenac by these materials is obtained at different time intervals from 5 to 120 min and different diclofenac initial concentration (from 5 to 100 mgL^{-1}). The adsorption experiments are conducted at constant pH ≈ 7.0 and temperature 295 K. Results are presented as adsorption capacity (mgg^{-1}) as a function of time (min) and initial DS concentration.

III. Results and discussion

III.1. Characterization of adsorbent

The X-ray pattern of MK10 (Fig.1) exhibited a typical reflection of montmorillonite that resulted in a basal distance (d001) at 10.26 Å. Further, the over visible diffraction peaks are, perhaps, due to the presence of some impurity. The X-ray pattern of MK10-C16 (Fig.1.b) is almost identical to its virgin MK10 (Fig.1.a) having with slight change in d-values and intensities of peaks.

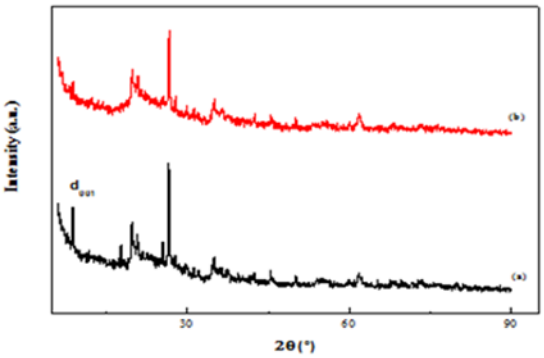


***Figure 1.** XRD pattern of (a) MK10 and (b) MK10-C16.*

III.2. Effect of contact time and initiale concentration on DS adsorption

Figure 2 illustates The effect of initial DS concentration (5-100 mgL-1) and the effect of contact time (5-120 min). The plot revealed that an increase in the DS concentration lead to an increase in removal quantity of DS, revealed the continoues capacity of this material to adsorbe DS.

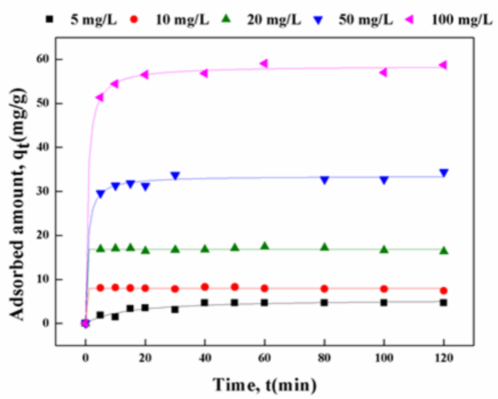


***Figure 2.** Effect of contact time and initial DS concentration on the removal of DS.*

III.3. Kinetics modelling

The kinetic data is further utilised in the kinetic modelling to estimate the rate constants along with

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the removal capacity of this adsorbent. Using a linear regression method, pseudo-first-order (PFO) expressed by (Eq. 1) [11] and pseudo-second-order (PSO) expressed by (Eq. 2) [12] kinetic models are used.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \textbf{(1)}$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{1}{q_e} t \qquad \textbf{(2)}$$

Where q_t and q_e are the amount of diclofenac removed at time't' and at equilibrium, respectively. k_1 and k_2 are the pseudo-first and pseudo-second-order rate constants, respectively. The estimated values of q_e, k_1 and k_2 are tabulated in Table 2. According to the correlation coefficient, results are best fitted to the PSO model. According to k_2 values; adsorption takes place in two stages: the first is fast, then the second is slow [13].

III.4. Adsorption Equilibrium Study

For adsorption equilibrium study: Langmuir, and Freundlich adsorption isotherms have been tested and were applied to describe the adsorption process of the experimental results. Linear form of Langmuir and Freundlich models can be expressed as [14, 15]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \textbf{(3)}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \textbf{(4)}$$

Where q_e is amount of diclofenac sodium adsorbed/ weight of adsorbent, K_L and q_m are the Langmuir coefficients. The intercept log K_F is a measure of adsorbent capacity and the slope *1/n* is the adsorption intensity.

The equilibrium adsorbate concentrations are important parameters which can affect the adsorption process considerably. The values monolayer capacity of adsorbent q_m, Freundlich constant K_F, *1/n* and R^2 are listed in Table 3. The value of the constant *1/n* is calculated to be 0.349. Since the value of *1/n* is less than 1, it indicates a favorable adsorption [16, 17].

Langmuir model fit the experimental data well, according to error functions. The Langmuir monolayer adsorption capacity was 63.33 mgg^{-1}, which is very promising compared with other organo-adsorbents for DS adsorption (Table 4).

Table 2. *Kinetic parameters estimated using PFO and PSO model for the removal diclofenac by MK10-C16 solid.*

C (mg/L)	Pseudo-first-order				Pseudo-second-order			
	q_e	k_1	h	R^2	q_e	k_2	h	R^2
5	3.79	0.0408	0.154		5.55	0.013	0.400	0.97
10	2.69	$1.68.10^{-4}$	0.0004		7.69	0.076	4.494	0.99
20	1.017	0.0061	0.006	<0.9	16.66	0.081	22.48	0.99
50	5.10	0.0161	0.082		34.48	0.027	32.09	0.99
100	10.59	0.258	2.732		58.82	0.023	79.57	0.99

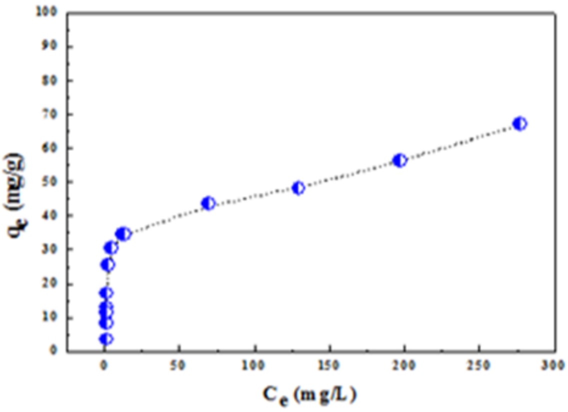

Figure 3. *Adsorption isotherm of DS onto MK10-C16.*

Table 3. *Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of DS on prepared samples.*

Model	Parameters	MK10-C16
Langmuir	q_m *(mg/g)*	63.33
	R^2	0.97
	K_L (dm^3/mg)	0.182
Freundlich	$1/n$	0.349
	R^2	0.71
	$K_F (mg/g\ (dm^3/mg)^{1/n})$	2.77

Table 4. *Maximum adsorption capacities for Diclofenac removal by various organo-adsorbents.*

Adsorbents	q_{max} (mg g^{-1})	References
MK10-C16	63.33	This work
Organo-bentonite (BH)	18.99	[18]
Organo-collected clay (LCH)	7.99	[18]
BH pillered with aluminium (BAH)	13.99	[18]
LCH pillered with aluminium (LCAH)	5.49	[18]
HDTMA modified zeolitic tuff	0.826	[19]
HDTMA modified clay	0.88	[19]
HDTMA-Mt	52.51	[20]

The maximum adsorption capacity of diclofenac was compared with other organo-adsorbents. From Table 3, we can see that obtained adsorption capacity value in this study is considerable comparing to other reported organo-adosorbents. The comparison shows that the organo-K10 montmorillonite used in this research shows a favorable adsorption capacity for diclofenac sodium. The high performances of diclofenac uptake could be explained by the organophilic behavior of synthesized adsorbent toward organic compounds such as diclofenac.

IV. Conclusion

The uptake of diclofenac by MK10-C16 is extreamly efficient as within 2 min of contact. An apparent equilibrium is achieved by MK10-C16 whereas within 5 min of contact. The obtained results indicated that the pseudo-second-order model fits the experimental data suitably well. The batch data implies that a very high uptake of diclofenac by MK10-C16 is very affected with increase in DS concentration. Langmuir adsorption isotherm model showed the best fit with the experimental adsorption data. The Langmuir monolayer adsorption capacity was 63.33 mgg^{-1}. MK10-C16 is found to be useful in the effective and efficient removal of diclofenac from aqueous solutions.

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