ADVANCES IN WATER TREATMENT BY ADSORPTION TECHNOLOGY: APPLICATION TO THE REMEDIATION OF POLLUTED WATER BY ANIONIC DRUG

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ABSTRACT

Diclofenac sodium (DS) is considered as priority anti-inflammatory pollutant because of its presence in water. In this paper, we addressed the issue of using organo-K10 montmorillonite as adsorbent of DS to reduce its negative effects on the environment. An organo-K10 montmorillonite (MK10-C16) was prepared by intercalating the organic cation cetyltrimethylammonium bromide (C16) in a K10 montmorillonite (MK10), and then characterized using XRD analytical technique. The organo-K10 montmorillonite displayed enhanced affinity for the DS in water. The results revealed that the rate of adsorption decreased with increase in temperature. 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.

Key Words: *Adsorption, Diclofenac Sodium, Organo-K10 Montmorillonite, Water.*

NOMENCLATURE

Symbols :

S_{BET} surface area, m²g^{-1}

CMC Critical Micelle Concentration, mM

pH potential hydrogen

T temperature, K

t time, min

M molar mass, gmol^{-1}

d basal distance, Å

q adsorbed quantity, mgg^{-1}

k_1 Pseudo-first-order constant, Lmin^{-1}

k_2 Pseudo-second-order, gmg^{-1}min^{-1}

q_m adsorption capacity, mgg^{-1}

n Freundlich constant

K_F Freundlich coefficient, mgg^{-1} ((dm³/mg)1/n)$^{-1}$

h speed of adsorption, mgg^{-1} min^{-1}

R^2 correlation coefficient

C massic concentratio, mgL^{-1}

K_L Langmuir coefficient, dm³mg^{-1}

Indices / Exponents :

e equilibrium

t at time t

1. INTRODUCTION

Drugs are deliberately designed to affect biochemical and physiological functions of biological systems in humans and livestock, their presence in environment means that they may elicit biochemical and physiological changes in soil and aquatic organisms. A recent survery en European river waters revealed that diclofenac ; an acidic pharmaceutical compound which belongs to the non-steroidal anti-inflammatory drugs (NSAIDs) family, is detected in 83% of collected samples [1]. Therefore, diclofenac is one of the top 10 compounds most commonly found in aquatic environments, due to its high level of consumption. It hase been detected in drinking water in many countries at µg-ng L^{-1} concentration levels [2]. Continued intake of diclofenac, even at low levels, by human shows several adverse biochemical effects (e.g., cytotoxicity to liver, kidney and gill cells as well the renal lesions) [3-7].

There is growing interest in the study and development of new adsorbents applicable to the remediation contaminated water. Water contamination by transport of pollutants from the adjacent environmental compartments would involve the application of treatments for decontamination that are usually complicated, lengthy, expensive, and often not feasible. The research of new adsorbents is a strategy to remediate the contamination of water produced by humain activities. In addition, application of environmentally friendly adsorbents into natural systems is particularly important to entail minimal environmental impact.

The aim of this work was to prepare and characterize an organo modified K10 montmorillonite, consisting of K10 montmorillonite intercalated with cetyltrimethylammonium bromide cations. Once synthesized, the most novel aspect of this work lied in the assessment of the removal of DS from water using the organo-K10 montmorillonite.

2. EXPERIMENTAL METHOD

2.1. Materials

K10 montmorillonite (MK10) (S_{BET}= 220-270 m^2g^{-1}), Cetyltrimethylammonium bromide (C16) (CMC= 0.92 mM) and diclofenac sodium (M=318.13 $gmol^{-1}$) were supplied by Sigma–Aldrich. The other chemicals are used of analytical or equivalent grades.

2.2. Methodology

2.2.1. Preparation of organo-K10 montmorillonite

The organo-K10 montmorillonite is obtained by cation exchange by C16 in an acidic medium according to Tiwari et al. [8].

2.2.2. Characterizations

X-ray diffraction (XRD) data is recorded using an X-ray diffraction machine (Bruker Advanced X-ray). The Cu Kα radiations having wavelength 1.5418 Å is used for X-ray diffraction analysis.

2.2.3. Batch reactor experiments

A stock solution of diclofenac sodium 1 gL^{-1} is prepared; dissolving diclofenac sodium into distilled water. The solubility is enhanced with the sonication of solution mixture for 24h. Further, the

required diclofenac concentration (from 10 to 500 mgL^{-1}) is obtained by successive dilution of stock solutions. The pH is adjusted using HCl/NaOH solutions. 50 mg of solid sample is introduced with these solutions. The bottles are kept in an automatic incubator shaker for 2 h at 295 K. These bottles are then taken out from the shaker, centrifuged and filtred with filter paper. The filtrates are then subjected to its bulk diclofenac concentration using UV-Visible spectrophotometer (Model: UV PharmaSpec-1700 UV-Visible spectrophotometer Shimadzu). The absorbance is recorded at 276 nm. The calibration curve is obtained using previously prepared standard diclofenac solutions having concentrations from 2 to 20 mgL^{-1}. Time dependence sorption of diclofenac by these materials is obtained at different time intervals from 5 to 120 min. The diclofenac concentration (from 5 to 100 mgL^{-1}) with solid dose 1 gL^{-1} is taken as constant and the sorption 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).

3. RESULTS

3.1. Characterization of materials

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.
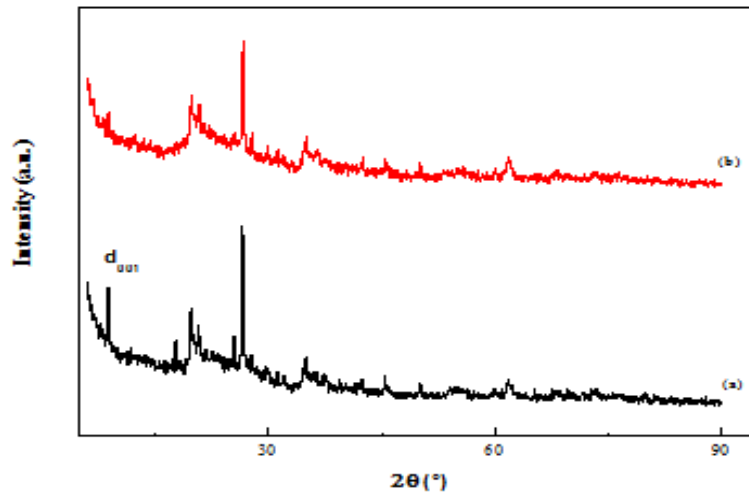

FIGURE 1. XRD pattern of (a) MK10 and (b) MK10-C16

3.2. Batch reactor operations

3.2.1. Effect of contact time on DS adsorption

The kinetic data is further utilised in the kinetic modelling to estimate the rate constants along with the removal capacity of these solids. Pseudo-first-order (PFO) expressed by (Eq. 1) [9] and pseudo-second-order (PSO) expressed by (Eq. 2) [10] kinetic models are used.

$$Ln(q_e - q_t) = ln\ q_e - k_1 t \qquad (1)$$

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

Where q_t and q_e are the amount of diclofenac removed at time't' and removal capacity 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 1. Results are best fitted to the PSO model comparing to the PFO model. For the kinetic model of the PSO, it can be noticed that the adsorption capacity q_m and the speed of adsorption h increases with the increase of DS initial concentration from 5 to 100 mgL^{-1}. Furthermore, we note the decrease in k_2 values; adsorption takes place in two stages: the first is fast, then the second is slow [11]. The values of the correlation coefficients are 0.99, superior to those obtained upon application of the first-order kinetic model.

C	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

TABLE 1. KINETIC PARAMETERS ESTIMATED USING PFO AND PSO MODEL FOR THE REMOVAL DICLOFENAC BY MK10-C16 SOLID

3.2.2. Adsorption isotherm

Several models have been used in the adsorption studies to describe the experimental data adsorption isotherms. Langmuir and Freundlich isotherms are the most frequently used models. Both models were investigated in this work.

Using a method of linear regression, the adsorption data has been fitted to Langmuir [12] adsorption model to describe the adsorption processes between solid-liquid interface :

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

$$q_e = (C_0 - C_e).\frac{V}{m} \tag{4}$$

Where q_e is amount of diclofenac sodium adsorbed/ weight of adsorbent, K_L and q_m are the Langmuir coefficients.

The Freundlich isotherm is a special case for heterogeneous surface energy in which energy in the Langmuir equation varies as a function of surface coverage strictly due to variation of adsorption [13]. The Freundlich adsorption isotherm can be expressed [14] as :

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

Where 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 2. 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 [15,16].

Both Freundlich and Langmuir model fit the experimental data well, but Langmuir isotherm was better according to error functions. The Langmuir monolayer adsorption capacity was 63.33 mgg^{-1}, which is very promising compared with other adsorbents for DS adsorption.
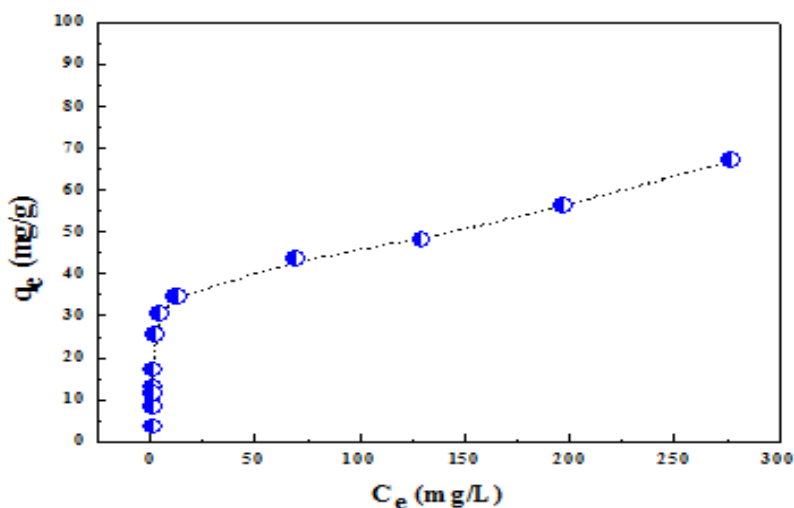
FIGURE 2. Adsorption isotherm of DS onto MK10-C16

Model	Parameters	MK10-C16
Langmuir	q_m	63.33
	R^2	0.973
Freundlich	$1/n$	0.349
	K_F	2.77
	R^2	0.711

TABLE 2. Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of DS on prepared samples

4. CONCLUSIONS

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 mg/g. MK10-C16 is found to be useful in the effective and efficient removal of diclofenac from aqueous solutions.

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