Adsorption of chlorhexidine digluconate on acid modified fly ash: Kinetics, isotherms and influencing factors

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ABSTRACT

Chlorhexidine digluconate (CHD) in the aquatic environment causes irreversible change to microbes, making them resistant to biodegradation, which needs remediation other than biological process. Adsorption study was performed for the removal of CHD on fly ash (FA) as a function of pH and ionic strength. Experimental result has been validated by characterization using Scanning electron microscopy, Fourier Transform-Infrared Spectroscopy and Brunauer-Emmett-Teller. CHD adsorption with FA showed an increasing trend with an increase in pH. Variation in pH proved to be an influential parameter for the surface charge of adsorbent and the degree of ionization of the CHD molecules. The adsorption capacity of CHD decreased from 23.60 mg g⁻¹ to 1.13 mg g⁻¹, when ionic strength increased from 0 to 0.1 M. The adsorption isotherms were simulated well by the Freundlich isotherm model having R² = 0.98. The Lagergren's model was incorporated to predict the system kinetics, while the mechanistic study was better explained by pseudo-second order for FA. On the basis of operational conditions and cost-effectiveness FA was found to be more economical as an adsorbent for the adsorption of CHD.

Keywords: Adsorption, Chlorhexidine digluconate (CHD), Fly ash, Isotherm and Kinetics

1. Introduction

Among the water pollution issues, pharmaceutical and personal care product have attracted more and more attention as novel emerging contaminants by the scientific community and common public as well [1]. High pollution load to the aquatic ecosystem contains oodles of disinfectant and antibiotics such as Diclofenac, Naproxen, Ibuprofen, Sulfamethazine, Sulfamethoxazole, Sulfathiazole and Chlorhexidine Digluconate (CHD) [2]. The disposal and degradation of such persistent pollutants by natural means are a difficult attempt, although they affect water quality and potentially impact drinking water supplies [3]. CHD (Fig. S1) is cationic molecules [1,6-bis (4-chloro-phenylbiguanido) hexane], a widespread antimicrobial agent used extensively in dentistry and veterinary such as mouthwash, toothpaste, skin cleanser and some pre-operative skin preparation, frequently used in daily life. The widespread incorporation of CHD in a vast array of pharmaceutical and personal care product results in direct discharge into the aquatic environment after their use [4]. Presence of CHD in the aquatic system at higher and lower concentration reported as "bacteriostatic agent" and "bactericidal agent", making them resistant to biodegradation [5]. Stability of

CHD molecules is also cramped due to its byproduct formation *p*-chloroaniline, which has rapid adsorption and metabolizing property, being hemotoxic and carcinogenic [6-7]. Therefore, the content of *p*-chloroaniline in mouthwash and the use of CHD at higher concentration limited by Pharmacopeias [8]. Moreover, CHD has been selected as a target compound due to its accumulation in the aquatic environment, affecting the aquatic life, sewage micro-organisms as well as drinking water quality [6].

The mode of action and mechanism of pharmaceutical waste (PhW) and personal care products (PCPs) in the aquatic ecosystem is tremendously uncertain. They are pervasively connected to their action on molecules, cells, lymphatic organs and human health [6]. Composition and quantity of wastewater generated from the pharmaceutical industries play a crucial role in their treatment. Several treatment methods such as chemical oxidation, photolytic, photocatalytic treatment, biodegradation can be used to remove a wide array of pollutant generated from the pharmaceutical industry [9-11]. These treatment methods have some drawbacks such as high cost, generation of a residual or secondary pollutants or by-products, longer duration of treatment and insufficient removal efficiency, limiting the use of these treatment technologies [9].

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Received November 23 2018 Accepted March 7, 2019

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Conversely, numerous favorable features of adsorption processes such as efficiency, simplicity, the capability of trace pollutant removal and no further by-product formation made it an alternative method for removal of PhW and PCPs. Adsorption could be easily scaled up from a laboratory to an industrial application with high removal efficiency [12-15].

The most commercialized adsorbent is activated carbon (AC) that has been used for the past few decades. But regeneration and cost effectiveness play a major role in the use of AC on large scale is difficult. Fly ash (FA) has received remarkable attention to overcome the cost-related problem. FA modified as a new low-cost AC due to its porosity, sphericity, high strength, non-toxicity and light weight property [16]. Use of FA as an adsorbent has dual benefit: i) removal of pharmaceutical and PCPs from the aquatic environment and ii) also maintaining the sustainability of the thermal power plant by-product generation [17]. Experimental pH and alkaline condition of wastewater generated from the pharmaceutical industry play a key role in the selection of adsorbent [18-19]. Easy availability of FA for the adsorption process prompts sustainable treatment technology as compared to the use of AC.

Adsorption of personal care product including CHD using traditional adsorbents (AC) has been well proved as it could not cause any by-product formation during adsorption, but the adsorption of compounds like CHD with AC needs pH modification of wastewater of pharmaceutical industry before adsorption process. The effluent from the pharmaceutical industry is well known for their alkaline nature and pH modification before treatment will cause economic and environmental complication. To overcome this issue the FA has been modified accordingly to achieve adsorption of CHD in alkaline condition. To understand the adsorption mechanism of modified FA, isotherm and kinetics studies were carried out and the property of adsorbent was examined by SEM, FTIR and Brunauer-Emmett-Teller (BET) analysis.

2. Materials and Methods

2.1. Chemicals and Sample Preparation

Standard solution of CHD (20% w/v) was purchased from Sigma-Aldrich. AC derived from charcoal, Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Sodium chloride (NaCl) was procured from Merck, India. Dissolved accurately weighed standard solution of CHD in 1 L of Milli-Q, RO water (Millipore, USA) to prepare 1,000 mg L⁻¹ CHD stock solution and serial dilution of the samples were carried for the lower concentration. FA was collected from Maithon Power Plant, Jharkhand.

2.2. Adsorbent and Their Characterization

In the present study, the FA was collected and sieved into a fine powder product and samples were washed number of times with warm distilled water (333.15 K) to remove the impurities. Chemical washing of FA was performed by 10% concentrated sulfuric acid using vacuum filtration system followed by washing with distilled water and kept in the oven at 383.15 K for drying and activation before using it as an adsorbent [20]. The chemical constituents of FA having SiO₂ (74.14%), Al₂O₃ (22.77%), Fe₂O₃ (1.244%), CaO

(1.19%), MgO (0.612%), and Na₂O (0.034%) was used in the present study. The BET surface area and porosity analyzer (Autosorb-1C, Quanta chrome, USA) were used to obtain surface area, pore size and pore volume under the influence of nitrogen gas at particular temperature 77.3 K. The surface morphology and topography of the adsorbent were studied using a FESEM (Zessis, Germany). FTIR spectrophotometer (Perkin Elmer) was used to determine the presence of the functional groups on the surfaces of the adsorbent, participated in the adsorption process.

2.3. Batch Experiment for Adsorption

The adsorption experiments were carried out in 250 mL Erlenmeyer flasks by mixing 0.2 g L⁻¹ of FA with 100 mL of pharmaceutical synthetic wastewater, containing different amount of CHD (ranging from 10 ppm - 500 ppm). The agitation speed of the mixture was maintained at 200 rpm in orbital rotator shaker (Remi Shaker incubator, CIS-24 PLUS) at a range of 293.15-308.15 K for 60 min. The pH (Hanna, India) of the solution was adjusted with 1 N NaOH or 0.1 N HCl solutions. The samples were then filtered through a filter paper (Whatman filter paper 42), and the concentration of CHD in the filtrate was estimated spectrophotometrically, at 275 nm using a UV-Vis spectrophotometer (Lab Tech 9100A, China).

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

Where, C_i is the initial concentration of CHD in the solution (mg L⁻¹), C_t is the concentration of CHD (mg L⁻¹) at time t .

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2)$$

Where, C_o is the initial concentration of CHD in the solution (mg L⁻¹), C_e is the concentration of CHD (mg L⁻¹) at time t , V is the volume of solution (L) and m is the mass of adsorbent (g), q_e (mg g⁻¹) is the adsorption capacity at time t .

3. Results and Discussion

3.1. Selection of Adsorbent

To understand the working pH during adsorption process, the "pHpzc" analysis was carried out for both the adsorbents and found 4.5 and 7.0 for AC and FA, respectively (Fig. S2 and S3). The "pHpzc" value for FA was found more favourable for adsorption of a selected pollutant, i.e. CHD as it has cationic property. The working pH of FA as an adsorbent was observed 8.5 which support the adsorption of CHD without further modification in the pH of wastewater. Keeping this fact, further study for AC was not investigated, and a detailed study was carried out with FA.

3.2. Characterization of Adsorbent

The surface morphology of the adsorbent before and after adsorption at the same magnification power has been shown in Fig. 1(a) & (b). Large open pores, irregular and heterogeneous surface of adsorb-

Fig. 1. Surface morphology of adsorbent (a) before CHD adsorption and (b) after CHD adsorption; (FA).

ent before adsorption (Fig. 1(a)) supported the influencing characteristics of adsorbent material. However in Fig. 1(b), smooth surface morphology was observed after adsorption, which confirmed the adsorption process and deposition of the CHD on the adsorbent.

The specific surface area of FA was found $0.744 \text{ m}^2 \text{ g}^{-1}$, respectively, using the BET equation. The classification of adsorbent pores were classified on the basis of their diameter into micropores ($< 2 \text{ nm}$), mesopores ($2\text{-}50 \text{ nm}$) and macropores ($> 50 \text{ nm}$) according to the International Union of Pure and Applied Chemistry (IUPAC) and the average pore width of FA was 2.3 nm ensuring it as a slightly mesoporous material due to unavoidable Vander Waal force [21]. This mesoporous structure of FA supported the accessibility of pollutants to the active sites, enhancing the adsorption process.

Fig. 2. Fourier Transform Infrared Spectroscopy of adsorption of CHD before and after onto (A) and (B) FA.

FTIR is a paramount technique to a qualitatively determine the functional group, which ensure the adsorption process. The FTIR spectra for FA before and after adsorption are shown in Fig. 2. The band observed at $1,088.65 \text{ cm}^{-1}$ and 767.01 cm^{-1} before adsorption were assigned as quartz and α quartz, respectively, while the band near 450.30 cm^{-1} and $2,923.71 \text{ cm}^{-1}$ ascribed as Si-O-Si bending and organic carbon, respectively in FA before adsorption, which confirms the basic properties of FA as an adsorbent [22-23]. The band within $800\text{-}400 \text{ cm}^{-1}$ and $850\text{-}950 \text{ cm}^{-1}$ ascribed as the occurrence of C-X stretching and the C-H stretching group in the organic compound [24]. There was a shift in the bands after adsorption of CHD on FA in the range of $800.7\text{-}897.72 \text{ cm}^{-1}$ revealed that the adsorption process of CHD on FA. Lastly, the band present at $1,414.89 \text{ cm}^{-1}$ in FA after adsorption has been ascribed to the presence of hydrocarbon revealing sorption of CHD over FA [16].

3.3. Effect of pH on CHD Adsorption

Experimental results revealed that the maximum removal efficiency of CHD was 77.5% at pH 8.5 as shown in Fig. 3(a). To optimize the removal percentage and pH, adsorption experiment was conducted in the pH range of 2.5-10.5 and the removal percentage varied from 13.67% to 77.23% as shown in Fig. 3(a). The result indicated that dissociation constant and pH play a crucial role in the adsorption of CHD onto FA, as dissociation of CHD molecules can be affected with change in pH. CHD molecules are expected to be protonated at $\text{pH} < \text{pK}_a$ ($\text{pK}_a = 10.8$), which dominates the cationic form of CHD in solution and $\text{pH} > \text{pH}_{\text{pzc}}$ ("pHpzc" of FA = 7.0), also confirmed the negative charge on the surface of FA. The results revealed that the adsorption capacity increased due to electrostatic interaction among highly protonated CHD molecules and negatively charged FA [25]. The FA comprised of metal

oxide that forms an aquo complex with water, and negative charge density on surface of adsorbent increased at $\text{pH} > \text{pH}_{\text{pzc}}$ of FA, which would further increase the removal efficiency due to the electrostatic interaction, whereas acidic medium ($\text{pH} < \text{pH}_{\text{pzc}}$) does not favor the removal of cationic adsorbate species as dissociation of CHD molecules suppressed by the presence of H^+ [26]. Conversely, as pH increased the amino group of CHD molecules are protonated, and the surface of adsorbents were deprotonated, which attributed more adsorption of CHD at moderately alkaline condition due to the electrostatic interaction between the positively charged adsorbate and negatively charged adsorbent [25].

3.4. Effect of Ionic Strength on CHD Adsorption

The adsorption capacity of CHD onto FA was significantly decreases from 23.60 mg g^{-1} to 1.13 mg g^{-1} , when ionic strength increased from 1×10^{-3} to $5 \times 10^{-1} \text{ M}$ as shown in Fig. 3(b). According to the literature, electrical double layer present around the surface of an adsorbent and CHD molecules which supports the binding of adsorbate to the adsorbent due to electrostatic interaction [27]. Compression of double layer occurs with an increase in ionic strength of the solution which reduces the thickness of the double layer according to the theory on diffuse double layer given by Gouy-Chapman. The gradual decrease in the adsorption capacity of FA was observed when the ionic strength increased; this might be due to competition between counter ions or consequent compression of electrical double layer present on the surface of FA due to electrostatic interaction made by chloride ion that further leads to more adherence of CHD with the water molecules [28-30]. Therefore, increase in the concentration of NaCl increased the bonding between CHD and FA, this leads to decrease in the adsorption of CHD by pairing their charges, and this initiated the adsorbent to sorb more positive CHD ions [31].

However, FA showed maximum adsorption at pH 8 with an increased concentration of ions. This indicates that at pH 8, the effect of pH is predominant compared to ionic strength due to

the cationic form of CHD and negatively charged surface of the adsorbent. This leads to a very high electrostatic attraction between CHD and adsorbent. A similar work about the effect of ionic strength on the adsorption of personal care product on different adsorbent was observed [31].

3.5. Isotherm Study of CHD

The adsorption isotherm studies provide significant information of adsorption capacity, adsorption properties and affinity of the adsorbent. Adsorption experiments have been performed at a constant dose, pH and time, whereas the initial concentration of the pollutant was varied. Two isotherm models namely Langmuir and Freundlich models were applied to examine the adsorption equilibrium by non-linear modelling. Non-linearized form of the Langmuir and Freundlich model can be written as following equations [32].

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad (3)$$

$$q_e = K_F C_e^{1/n} \quad (4)$$

Where, the equilibrium concentration of CHD (mg L^{-1}) is defined by C_e , q_e is the amount of CHD adsorbed at equilibrium (mg g^{-1}), Q_o is the maximum monolayer adsorption capacity of adsorbent (mg g^{-1}) and b is the Langmuir adsorption constant (L mg^{-1}), K_F and n are the Freundlich constants incorporating the factor affecting adsorption intensity and adsorption capacity, respectively. The Langmuir and Freundlich isotherm plots discussed in Fig. 4 showed the relationship between the equilibrium constant (C_e) and adsorption capacity (q_e) due to CHD uptake of prepared aqueous solution for FA at 303.15 K. The graph plots among experimentally calculated values of $1/q_e$ versus $1/C_e$ (Langmuir isotherm), $\text{Log } q_e$ versus $\text{Log } C_e$ (Freundlich isotherm) at different temperature were made using origin pro 8.5.0SRI and best-fit values of parameters were determined. The values of the isotherm

Fig. 3. Effect of solution (a) pH and (b) Effect of ions on CHD adsorption onto FA ($C_0 = 10 \text{ mg/L}$, adsorbent dose = 0.2 g/L).

Fig. 4. Plot of C_e versus q_e (a) Langmuir; (b) Freundlich isotherm of CHD adsorption on fly ash at 303.15 K.

Table 1. Calculated Isotherm Parameters for Langmuir and Freundlich Models for Adsorption of Chlorhexidine Digluconate onto Fly Ash at Various Temperature

Adsorbent	Temperature (°C)	Langmuir isotherm			Freundlich isotherm		
		Q_m	K_L	R^2	K_f	n	R^2
Fly ash	20°C	19.7	17.5	0.58	5.5	2.2	0.59
	25°C	61.3	0.012	0.92	2.4	1.4	0.96
	30°C	47.01	0.0334	0.91	5.5	2.4	0.98
	35°C	30	0.0048	0.90	2.45	2.15	0.90

constants and correlation coefficient, R^2 for the best-fit of the equations have been listed in Table 1.

The regression coefficient (R^2) is deemed to serve as a reliable statistical metric for the determination of quality fitness from the data obtained from applying an isotherm model [22]. Furthermore, the regression coefficient (R^2) also serves as a reliable metric for comparing the efficacy of different isotherm models. It was observed that the Freundlich model ($R^2 = 0.98$) showed a better regression coefficient than the Langmuir model, thus ascertaining adsorption of CHD onto FA, for all the temperatures. This showed the heterogeneous distribution of CHD on the active site of adsorbent and thus leads to multilayer formation [22]. From the models (both Langmuir and Freundlich), a consistent affinity towards the adsorption of CHD on FA was deduced from the test for Freundlich isotherm.

3.6. Kinetic Studies of CHD

The kinetic model used to establish the adsorption mechanisms

as well as possible rate controlling steps and equilibrium concentration as a function of time. The kinetics of the adsorption system was studied using pseudo-first order [33] and pseudo-second order [34], expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$t/q_t = \frac{1}{k_2 q_e^2} + \frac{1(t)}{q_e} \quad (6)$$

Where, q_e is the amount of CHD adsorbed at equilibrium (mg g^{-1}) and q_t is the amount adsorbed at time t and the constant rate for pseudo-first order sorption (min^{-1}) is denoted by k_1 . The kinetic parameter for these two models was calculated from Eq. (5) or (6). From Fig. 5 and calculated parameter in Table 2, the kinetic rate was well simulated by the pseudo-second order having R^2 value 0.93. The results revealed that the adsorption of CHD onto FA was dominated by the pseudo-second order model,

Table 2. Parameters for Two Kinetic Model of CHD Adsorption

Adsorbent	Model	Parameter	Value
Fly ash	Pseudo-first order: $\ln(q_e - q_t) = \ln q_e - k_1 t$	$k_1 (\text{min}^{-1})$	0.075
		R^2	0.8671
	Pseudo-second order: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1(t)}{q_e}$	$k_2 (\text{mg/g/min}^{-1})$	0.182
		R^2	0.9368

Fig. 5. Fitting curves of (a) pseudo-first order kinetic model and (b) pseudo-second order for FA dosage of 0.2 g/L at; pH-8.5, CHD concentration -50 mg/L for 60 min.

which indicating that chemisorption involving valance force through the exchange or sharing of electrons controlled the adsorption rate [35].

3.7. Regeneration Study

Regeneration capacity is one of the important criteria for the selection of adsorbent and to understand the stability of the selected adsorbent, i.e. FA. The regeneration study was carried out, and a significant amount of CHD (60.08%) desorption was observed after the third cycle. Considering FA as an adsorbent for the removal of CHD from aqueous solution showed promising regeneration potential of the selected adsorbent.

4. Conclusions

The H_2SO_4 -activated FA showed a good adsorption capacity for CHD removal in alkaline conditions. The experimental data were best described by the Freundlich isotherm model with the highest R^2 value (0.98), which confirmed the multilayer of the adsorbent surface. The kinetic study suggested that the pseudo-second order model was best fitted for FA and indicated the chemisorption mechanism for the adsorption process. The influence of ionic strength on the population of functional adsorbent sites shows proportionate participation in the ion-exchange of CHD compounds on modified FA. Overall, the favorable operational conditions during the adsorption process of FA could be the best choice for controlling the transport of CHD and other personal care product similar to CHD in the aquatic environment.

Acknowledgments

The authors would like to acknowledge Indian Institute of Technology (Indian School of Mines), Dhanbad, India, for providing research and financial facilities. The authors declare no conflict of interest.

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