Asian Journal of Research in Chemistry
(Home.aspx)

ISSN
0974-4150 (Online)
0974-4169 (Print)

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DOI: 10.52711/0974-4150.2022.00032 (https://doi.org/10.52711/0974-4150.2022.00032)

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Published In: Volume - 15, Issue - 3, Year - 2022 (Issues.aspx?VID=15&IID=3)

Keywords: Fixed bed column () Phenols () dyes () Breakthrough curves () Bed capacity. ()

Cite this article:
Samuel N. Ndung'u, Ruth N. Wanjau, Esther W. Nthiga. Fixed Bed Column Adsorption Studies of selected Phenols and Dyes using Low-cost adsorbents. A mini Review. Asian Journal of Research in Chemistry. 2022; 15(3):189-4. doi: 10.52711/0974-4150.2022.00032

Fixed Bed Column Adsorption Studies of selected Phenols and Dyes using Low-cost adsorbents. A mini Review

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ABSTRACT
Consumption of water contaminated with dyes and phenolic compounds is detrimental to human and animal wellbeing even at permissible limits. Therefore, their decontamination from water is important for the safety of consumers. Conventional water treatment techniques such as ozonation, ion exchange among others are expensive and ineffective. Adsorption as an emerging technique has gained research interest because of its ease in design, environmentally friendly and availability of materials as adsorbents in large quantities. The application of various adsorbents have extensively been reported for decontamination of dyes and phenolic compounds in wastewater such as 4-chlorophenol, Metanil Yellow (MY) dye, Phenol, Methyl green dye, Bromothymol Blue dye, Crystal violet, Methylene blue and Direct Blue 71. It has also been reported that adsorption by column continuous processes are more efficient than batch as it can be used continuously under high effluent flow rates in many pollution control processes in an industrial set up. The fixed bed column adsorption data is analyzed at different column conditions of bed height, pH, particle size, concentration and flow rate using different kinetic models such as Bohart-Adams, Thomas, Yoon-Nelson, Clark, Bed depth service time and Wolborska models amongst others to determine the column performance. The present paper involves a mini review of dynamics of fixed-bed column studies for removal of selected dyes and phenolics from a synthetic media.

Keywords: Fixed bed column, Phenols, dyes, Breakthrough curves, Bed capacity.

1. INTRODUCTION

Water is an essential resource for sustaining life to humans, plants and animals[1,2]. Streams, rivers and wells are source of drinking water for many rural folks[3]. However, these water sources are polluted due to rapid industrial advancements in our societies[4,5,6]. This has resulted to a continued discharge of toxic organic and inorganic pollutants such as heavy metal ions, dyes, phosphate compounds, phenolics amongst others into these water sources[7].

One of these organic pollutants of environmental concern are dyes and phenolic compounds[8,9]. Phenols are discharged to water bodies from industrial effluents of pharmaceuticals, petroleum refineries, pesticide manufacturing, paint production, paper and pulp industries amongst others[10,11]. A phenolic compound contain hydroxyl group(s) which are bonded directly to a benzene ring[12]. These hydroxyl groups dissociate easily in water forming stable phenolate ions[13]. Their presence in water bodies is toxic and detrimental to the ecosystem[14]. This makes quality of such drinking water questionable for use. Maximum limit for phenolics in drinking water is 0.1 ppm[15] beyond which such water is unsafe for consumption.

Synthetic dyes are introduced to water bodies via wastes from leather, printing, textiles, food processing, paper, plastics and cosmetic industries[8,16]. The rate at which they are discharged to aquatic environment is alarming and if not addressed can cause a serious environmental problem[17]. They are mutagenic, carcinogenic, toxic and non-degradable[6,18]. They also have complex aromatic structures[19] making it costly to treat such textile effluents using conventional decontamination technologies[4].

Different conventional processes have been employed for elimination of dyes and phenolics from wastewater are such as ozonation[20,21,22], ion exchange[23,24], precipitation[25], coagulation-flocculation[26], photocatalytic degradation[27,28,29,30], electrochemical methods[31,32] and adsorption[13,33]. Among them, adsorption technique have remained the most effective technique because of its effectiveness, simplicity and economical in water purification[34]. Low-cost adsorbents such as moroccan clay[35], olive stones[36], corn cobs[37], egg shell[38], baobab fruit shell[10] amongst others have been employed in the removal of various dyes and phenolic compounds. The paper presents a review of fixed-bed column studies of selected dyes and phenols using vast low-cost adsorbents.

2. COLUMN ADSORPTION STUDIES:

A packed bed column is a device that is packed with an adsorbent in which wastewater is passed through it and gets adsorbed onto the adsorbent surface[11]. It is more convenient in its applicability in an industrial scale that deals with high flow rates[39,40]. It is more preferred than batch due to its ease of operation, adoptability, flexibility, high liquid residence times and high removal efficiency with continuous operation[38,41,42]. The set-up for a fixed-bed column is given in Figure 1[43]:

Figure 1: A fixed bed column

Initially, there is rapid adsorption of the adsorbate due to less adsorbate available at the upper layers[44]. The adsorbent becomes saturated as the entire pores in the zone are completely occupied following previous adsorptions[45]. The adsorbate progresses to the un-adsorbed part of adsorbent in the column (mass transfer zone) where actual adsorption occurs[46]. Afterwards, the column is completely saturated and therefore, no adsorption[47]. At this point, the influent-effluent concentration ratio is 1. This generates a breakthrough curve summarized by figure 2 below[48]:

Figure 2: A breakthrough curve

A breakthrough curve is a plot of influent-effluent concentration ratio as a function of treatment time[4]. It is employed to describe the efficiency of column operations[46]. Breakthrough occurs when analyte of a certain influent concentration moves through the column at a certain period of time and leaves the column with a final concentration.

The various parameters such as the quantity adsorbed at breakthrough and at saturation times, removal efficiency, effluent volume, bed capacity, fractional bed utilization and mass transfer zone are determined to evaluate the column performance[11]. The bed capacity is determined using equations 1 and 2[38, 49] at breakthrough and saturation points respectively:

Where is the bed capacity at breakthrough time (mg/g), is the bed capacity at saturation (mg/g), m is the adsorbent mass (g). Q is the volumetric flow rate (mL/min), is the initial concentration (mg/L), C is the concentration at a time t, (mg/L), is the breakthrough time (min) and is the saturation time (min).

The total amount (q_{total}) adsorbed is determined from the area under the curve of adsorbed concentration (C_{ad}) versus time (t) multiplied by the flow rate, according to equation 3[50]:

Where F is the flow rate (mL/min); t_{total} is the total flow time (min); C_{ad} is the adsorbed concentration (mg/L).
The maximum bed capacity (q_{eq}) can be calculated from the equation 4[51]:

Where w is the amount of the adsorbent (g) and is total flow time (minutes).
The total amount (m_{total}) of the adsorbate pumped into the column is determined using equation 5:

Where, and Q is the total flow time (min) and volumetric inflow rate (mL/min), respectively[52].
The removal efficiency at breakthrough is determined by equation 6[53]:

The mass transfer zone is calculated using equation 7[54]:

Where and are breakthrough and saturation times respectively, Z is the length of the bed (cm).
The concentration of adsorbate that was not adsorbed at equilibrium in the column Ce (mg/L) is determined by equation 8[55]:

3. COLUMN ADSORPTION DYNAMICS:

The various parameters of flow rate, influent concentrations, bed height and particle size amongst others affect have an effect on the breakthrough curves[49]. The adsorption data from fixed bed column studies is analyzed at different column conditions using different kinetic models such as Thomas model, Adams -Bohart model, Yoon-Nelson model[56, 57], Clark model[58, 59], Wolborska model[34], bed depth service time[60] amongst others. They are discussed in the following sub-sections.

3.1 Thomas model:

The model assumes second order reversible kinetics and Langmuir isotherm adsorption[49]. It is employed to calculate the adsorption capacity of the adsorbent[61]. The linearized form of the model is given by equation 9:

(9)

Where is the model constant (L/mg h), is the maximum solid-phase concentration of solute (mg/g) and V the volume.

A plot of against time (t) yields a straight line used to calculate and [62].

3.2 Clark model:

The model assumes the Freundlich isotherm adsorption behavior and that the overall adsorption rate is determined by the mass transfer outside the adsorbate[38]. The linearized form of the model is given by the equation 10:

(10)

where and (mg/L) are the effluent and influent concentrations respectively; n is the Freundlich isotherm parameter; A and ω are Clark constants.

3.3 Yoon-Nelson model:

The model describes a decrease in probability of the analyte adsorbing on the adsorbent as being proportional to the possibility of its adsorption and breakthrough from the column system[43]. The model is a very simple as no detailed data concerning adsorbate features, adsorbent type and physical properties of the adsorbent bed[63]. Its linearized expression is given by the equation 11[19]:

(11)

where (min^{-1}) is the rate velocity constant, and τ (min) is the time required for 50% adsorbate breakthrough (i.e. $C_t/C_0 \approx 0.5$). The model parameters are determined from a linear plot of against time (t).

3.4 Adams-Bohart model:

The basis of the model is on the surface reaction theory to describe the initial part of the breakthrough curve[64]. The model assumes that equilibrium is non-instantaneous and that the rate of adsorption is proportional to the fraction of adsorption capacity[65]. The model describes a fundamental correlation between the normalized concentration (C_t/C_0) and the bed height (Z) summarized by the linearized equation 12[66]:

where t is the flow time (min), is the model kinetic constant (L/mg/min), is the maximum concentration at saturation (mg/L), Z is the bed height (cm), and is the superficial velocity (cm/min). A linear plot of against time (t) is used to calculate and from slope and intercept respectively.

3.5 Wolborska model:

The model explains the adsorption behaveior based on diffusive mass transport phenomena for low concentration phase of breakthrough plots[67]. Its linearized expression is given by the equation 13[62, 68]:

where is the kinetic coefficient of external mass transport (min^{-1}), is the superficial velocity (cm/min) and Z is the bed height (cm).

3.6 Bed depth service time model:

The model assumes that the rate of sorption is controlled by the surface reaction between the analyte and the unused adsorbent[69]. This model is used to predict the relationship between bed depth (Z) and the service time (t)[70]. Its linearized expression is given by the equation 14[71].

Where is the adsorption capacity (mg/g), and is the model rate constant (l/mg/min). A linear plot of bed depth (Z) against time (t) yields a straight line that is used to determine and .

The table below shows a summarized column adsorption kinetic modelling of experimental data for removal of selected phenols and dyes on different adsorbents:

Table 1: kinetic models for adsorption of selected dyes and phenols using low cost adsorbents

Adsorbent	Analyte	Optimum parameters	Bed capacity (mg/g)	Model	Reference
Nano graphene oxide	4-chlorophenol	Flow rate= 1 mL/min Concentration= 5 mg/L Bed height= 15 cm	145.2	Thomas Yoon-Nelson	56
Cassava peels (NaOH-Activated Carbon)	Metanil Yellow dye	pH= 5.32 Bed height= 10 cm Concentration= 100 mg/L Flow rate= 13.3 mL/min	4.12	Thomas, Yoon-Nelson and Clark	55
Corn Cob (Activated Carbon)	Phenol	Flow rate= 9 mL/min Particle size= 300 µm Concentration= 100 mg/L Bed height= 10 cm	8.570	Thomas, Adam Bohart Wolborska	49
Lantana camara Forest Waste	Phenol	Flow rate=15 mL/min Bed height= 10 cm Concentration= 150 mg/L	149.77	Thomas	11
Mesoporous materials (MCM-41)	Methyl green dye	Flow rate= 0.8 mL/min Bed height= 6 cm Concentration= 20 mg/L	20.97	Yoon- Nelson	72
Chitosan	Azo Dye	Flow rate= 0.8 mL/min Bed height= 8 cm Concentration= 100 ppm	6.80	Thomas Adams-Bohart Yoon-Nelson	63
Rice Husk (Activated Carbon)	Phenol	Bed depth= 7.5 cm Flow rate= 4.5 mL/min	28	Yoon Nelson Thomas	73
Magnetic Chitosan-Bamboo Sawdust	Bromothymol Blue acid dye	Flow rate= 20 mL/min Bed height= 5 cm	225.13	Thomas	74
Durian peel waste	Methylene blue	Bed height= 4 cm Concentration= 600 mg/L	235.80	Thomas	75

	Crystal violet	Concentration= 600 mg/L Flow rate= 10 mL/min	527.64		
Chitosan–glutaraldehyde	Direct Blue 71	Flow rate= 1 mL/min Concentration= 50 mg/L Bed height= 3 cm	343.59	Bed depth service time	4
Corn cob (Activated carbon)	Phenol	Bed height= 10 cm Initial concentration= 100mg/L Flow rate= 9mL/min Particle size= 300µm	8.570	Thomas, Adams-Bohart Wolborska	34

4. CONCLUSION:

From the reviewed work, it is evident that adsorbents such as Corn cob (Activated carbon), Chitosan, Durian peel waste, Rice Husk, Mesoporous materials (MCM-41), *Lantana camara* Forest Waste, Cassava peels and Nano graphene oxide are excellent in removal of dye and phenolics from aqueous solutions. Breakthrough curves at different process parameters of initial concentration, flow rate, bed height, pH and particle size are employed to design the column performance using different kinetic models such as Thomas, bed depth service time, Adams-Bohart, Wolborska, Yoon–Nelson and Clark.

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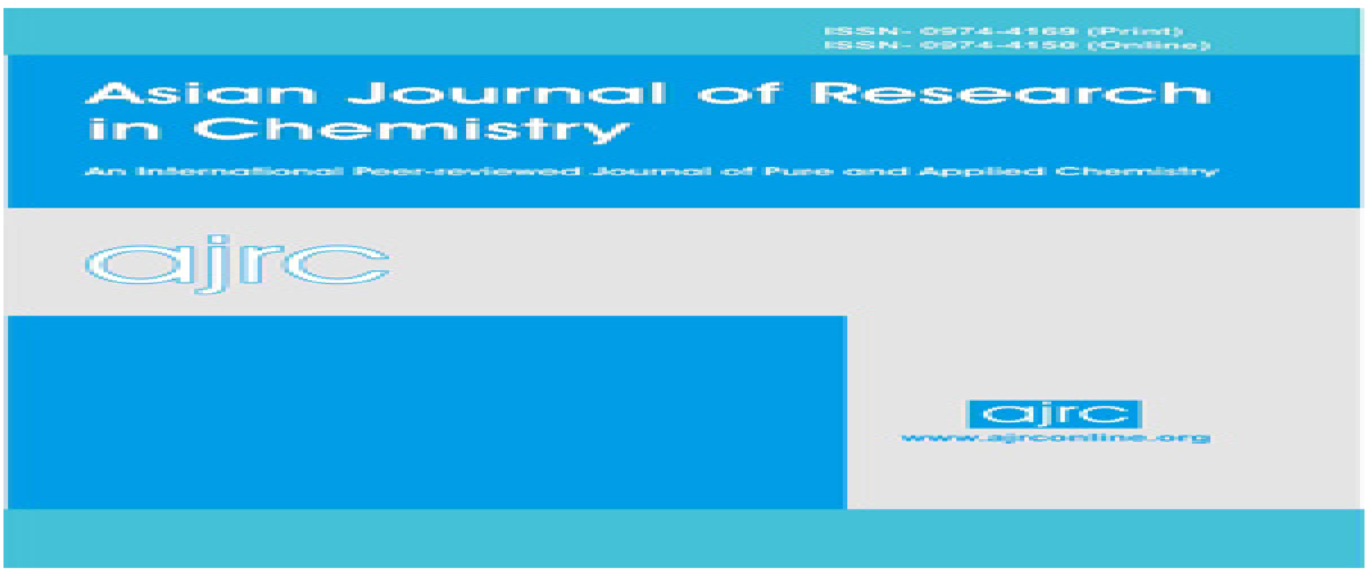

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