



An overview on the key advantages and limitations of batch and dynamic modes of biosorption of metal ions

Masamvu Malbenia John^a, Asmaa Benettayeb^{a,**}, Mohamed Belkacem^{a,b}, Chitepo Ruvimbo Mitchel^a, Mustapha Hadj Brahim^{a,b}, Imene Benettayeb^c, Boumediene Haddou^b, Saleh Al-Farraj^d, Abdullah Ali Alkahtane^d, Soumya Ghosh^{e,o,***}, C.H. Chia^f, Mika Sillanpää^{g,h,i,j}, Omirserik Baigenzhenov^k, Ahmad Hosseini-Bandegharai^{l,m,n,*}

^a Laboratoire de Génie Chimique et de Catalyse Hétérogène, département de Génie Chimique, Université de Sciences et de la Technologie -Mohamed Boudiaf, USTO-MB, BP 1505, EL-M'NAOUAR, 31000, Oran, Algeria

^b Laboratoire Physico-Chimie des Matériaux – Catalyse et Environnement – LPCM-CE, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf (USTO-MB), BP 1505, EL M'naouer, 31000, Oran, Algeria

^c Département d'automatique et Informatique Industrielle, Université de Sciences et de la Technologie -Mohamed Boudiaf, USTO-MB, BP 1505, EL-M'NAOUAR, 31000, Oran, Algeria

^d Department of Zoology, College of Science, King Saud University, Riyadh, Saudi Arabia

^e Natural & Medical Sciences Research Center, University of Nizwa, Nizwa, 616, Oman

^f Department of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia

^g Functional Materials Group, Gulf University for Science and Technology, Mubarak Al-Abdullah, 32093, Kuwait, Kuwait

^h Centre of Research Impact and Outcome, Chitkara University Institute of Engineering and Technology, Chitkara University, Rajpura, 140401, Punjab, India

ⁱ Division of Research & Development, Lovely Professional University, Phagwara, 144411, Punjab, India

^j Department of Chemical Engineering, School of Mining, Metallurgy and Chemical Engineering, University of Johannesburg, P. O. Box 17011, Doornfontein, 2028, South Africa

^k Department of Metallurgical Engineering, Satbayev University, Almaty, 050013, Kazakhstan

^l Faculty of Chemistry, Semnan University, Semnan, Iran

^m Department of Sustainable Engineering, Saveetha School of Engineering, SIMATS, Chennai, 602105, Tamil Nadu, India

ⁿ Chitkara Centre for Research and Development, Chitkara University, Himachal Pradesh, 174103, India

^o Department of Genetics, Faculty of Natural and Agricultural Sciences, University of the Free State, Bloemfontein 9301, South Africa

* Corresponding author. Faculty of Chemistry, Semnan University, Semnan, Iran

** Corresponding author.

*** Corresponding author. Natural & Medical Sciences Research Center, University of Nizwa, Nizwa, 616, Oman

E-mail addresses: asmaa.benettayeb@gmail.com, asmaa.benettayeb@univ-usto.dz (A. Benettayeb), soumyaghosh@yahoo.com (S. Ghosh), ahoseinib@semnan.ac.ir (A. Hosseini-Bandegharai).

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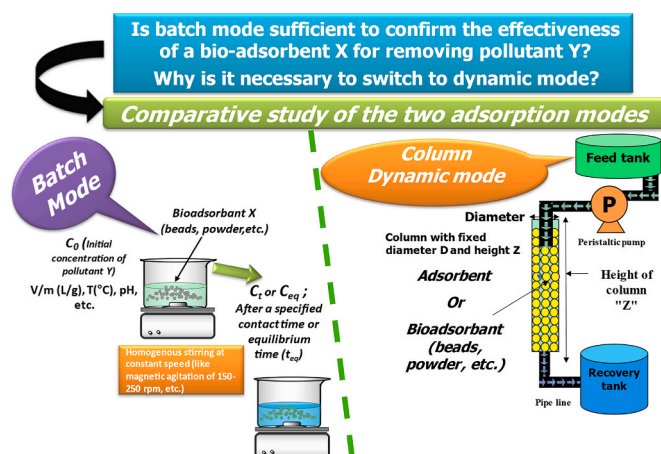
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HIGHLIGHTS

- Adsorption properties of batch and dynamic modes of biosorption were scrutinized in different conditions.
- The key advantages and drawbacks of each mode were mentioned.
- The benefits of exploitation of each mode were explained depending on the application purpose.
- Comparison between batch and dynamic modes of biosorption revealed limitations of the former.
- The switch to the dynamic mode seems to be necessary for practical applications.

GRAPHICAL ABSTRACT



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ABSTRACT

Water purification using adsorption is a crucial process for maintaining human life and preserving the environment. Batch and dynamic adsorption modes are two types of water purification processes that are commonly used in various countries due to their simplicity and feasibility on an industrial scale. However, it is important to understand the advantages and limitations of these two adsorption modes in industrial applications. Also, the possibility of using batch mode in industrial scale was scrutinized, along with the necessity of using dynamic mode in such applications. In addition, the reasons for the necessity of performing batch adsorption studies before starting the treatment on an industrial scale were mentioned and discussed. In fact, this review article attempts to throw light on these subjects by comparing the biosorption efficiency of some metals on utilized biosorbents, using both batch and fixed-bed (column) adsorption modes. The comparison is based on the effectiveness of the two processes and the mechanisms involved in the treatment. Parameters such as biosorption capacity, percentage removal, and isotherm models for both batch and column (fixed bed) studies are compared. The article also explains thermodynamic and kinetic models for batch adsorption and discusses breakthrough evaluations in adsorptive column systems. The review highlights the benefits of using convenient batch-wise biosorption in lab-scale studies and the key advantages of column biosorption in industrial applications.

1. Introduction

Various researchers have drawn attention to several types of environmental pollution from chemical and physical processes that affect both human life and the environment (water and soil) (Bhat et al., 2022a,b; 2021; Sher et al., 2021a,b,c; Yaqoob et al., 2021). Today, many researchers are involved in cleaning the environment from toxic organic and inorganic pollutants, developing various physicochemical and biochemical methods for the related purposes. For waters and wastewater treatment purposes and removal of heavy metal ions from such media, there are several traditional treatment methods which have been employed in the previous decades, including chemical precipitation (Cieszyńska and Wiśniewski, 2012; Gupta and Singh, 2013), electrochemical deposition (Al Aji et al., 2012; Chen, 2004), ion exchange for sorption from dilute effluents (Parodi et al., 2008), and membrane separation (Blöcher et al., 2003; Samper et al., 2009). However, cost, efficiency and secondary pollution limit the application of these traditional treatment methods. In this regard, adsorption technology and some other treatment technologies, such as electrocoagulation, seem to be the way out from these limitations and is a viable route for the treatment of metal ions-polluted waters and wastewaters (Benettayeb et al., 2017; Hocine et al., 2023; Kausar et al., 2017; Othmani et al., 2022; Sher et al., 2020, 2021b). The industry has always shifted towards the use of low-cost, less wasteful, and environmentally friendly methods that take up as little space as possible for adsorption effluent treatment

plants (Patel, 2019; Rashid et al., 2020). Therefore, the simplicity, being low-cost, and other advantages of adsorption technology have resulted in implementations of adsorption processes in effluent treatment plants in industries, since this technology take up as little space as possible and the ongoing research on it endlessly move towards devising methods with lower cost, less wasteful, and using environmentally-friendlier sorbents (Patel, 2019).

In fact, for all these advantages, during the past years, the adsorption technology has proven its advantages as an effective method for treating a range of heavy metals and some dyes in wastewater such as crystal violet (CV), Blue FBN (BFBN) and Rose FRN (RFRN), Cd(II), Pb(II), Hg (II) and Cu(II) (Benettayeb et al., 2021, 2021b; Ismail et al., 2024; Kausar et al., 2020; Wang et al., 2019).

These researchers have explained why adsorption/sorption is an effective process to eliminate various pollutants compared to other methods. They have pointed out the following advantages of the adsorption process: (1) Easy to operate and maintain, and low-cost for water treatment; (2) Simple design and speedy process; (3) High yield and potential for excellent performance, along with flexibility; and (4) Availability of diverse effective adsorbents that correspond to each specific pollutant.

In addition to synthesis of advantageous new adsorbents, some adsorbents are prepared from waste materials, like agricultural wastes. Biosorption with this category of sorbents even offers more advantages over traditional treatment methods, by bestowing higher cost-

effectiveness and exploiting biodegradable sorbents, because such adsorbents are available naturally and can be modified to enhance the adsorption of any type of pollutant (Benettayeb et al., 2021a; Benettayeb and Haddou, 2021). Fundamental mechanisms for uptake of metal ions by adsorption processes are ion exchange, complexation, chelation, surface sorption, and precipitation. These mechanisms are related to types of interactions involved between adsorbent and adsorbate and they also depend on the functional moieties existing on sorbent surface and adsorbate's features. For example, agricultural waste-based adsorbents have versatile functional groups (carboxyl, hydroxyl, amide, and amine), which make the biosorption process more efficient (Pang et al., 2011).

Even though research literature on batch sorption is highly available, there are few reports on using bio-adsorbents in dynamic mode (in a column) for elimination of metal ions from aqueous phases. Dynamic sorption is a continuous processing which involves the introduction of a contaminated solution into a column filled with sorbent/bioadsorbent. Batch experiments elucidate basic information about the characteristics of sorbent and factors affecting sorption processes (Kausar et al., 2017). Fig. 1 shows the statistics of existing searches on ScienceDirect in the period of 2020–2024 for dynamic mode and batch mode adsorption, using different keywords including "adsorption", "sorption", "elimination", "removal", "batch", and "dynamic". As it can be observed, a low percentage of adsorption studies are performed in dynamic mode compared to batch mode, i.e., 69.05% in batch mode (equivalent to +2086634 documents) vs. 935193 documents published in dynamic mode (30.95%) (Fig. 1).

The concept behind this review is new and innovative. It arose due to the challenges faced when transitioning from batch mode to dynamic mode in both laboratory and chemical industry settings. We have observed a decline in process efficiency and performance disruption, which is directly linked to the pollutant treated, process design and dimensions, as well as operating parameters. In addition, while selecting the best adsorbents for each pollutant is crucial in batch mode studies, we need to ask ourselves if these adsorbents behave differently in dynamic mode, particularly when applied in industrial conditions. Furthermore, there are various challenges in implementing the process, as any errors during the installation can result in inaccurate outcomes. Therefore, it is important to identify the critical parameters for achieving success in the batch adsorption mode (Amar et al., 2023; Benettayeb et al., 2017, 2024). Additionally, it is crucial to determine the key parameters for transitioning from batch to dynamic mode, and when scaling up to the chemical industry level.

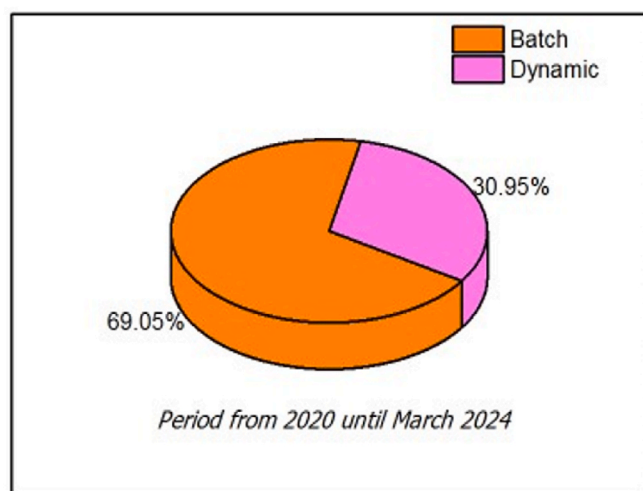


Fig. 1. Statistics of existing searches on ScienceDirect in the field of dynamic and batch modes of adsorption using different keywords including "adsorption", "sorption", "elimination", "removal", "batch", and "dynamic".

In terms of publications, it is worth noting that the number of papers published in dynamic mode is low worldwide. This is mainly due to the difficulties encountered in creating dynamic mode in comparison to batch mode. The purpose of this new review is to detect errors that occur during the application of dynamic adsorption mode, provide explanations to understand the best process performance in dynamic mode, and propose perspectives to avoid these errors. The review compares the performances of batch and dynamic sorption modes and critically examines the performances of various adsorbents for heavy metals removal by adsorption. Moreover, the review explains the factors that have an impact on batch adsorption, such as contact duration, pH, temperature, and adsorbent dosage. Additionally, it specifies the key factors to consider when switching to column adsorption, such as inlet concentration, flow speed, and height of the column. Furthermore, the review compares the isotherm and kinetic models for both adsorption modes. Finally, it mentions the better conditions for exploiting either of these two adsorption modes.

2. Definitions of the two modes of adsorption

Adsorption/sorption is a spontaneous surface process where molecules in solution bind in a condensed layer (or multilayer) on a solid or gel surface, altering its physical and chemical properties (Benettayeb et al., 2017; Hamza et al., 2022b). This phenomenon exhibits certain materials' abilities to bind ions or molecules to their surfaces more or less reversibly. These materials usually have porous structures and a large specific surface area. Biosorption is a subcategory of adsorption which is defined as the removal of metal ions from solutions by biological based-materials (like; chitosan, alginate, algae, moringa oleifera, gelatin, cellulose, bentonite, sheep waste, egg waste, etc.) (Benettayeb et al., 2022). Adsorption can be conducted in two modes, either in batch (discontinuous) or in column (continuous) mode.

2.1. Static regime (batch) adsorption

It is based on agitation of a known amount of sorbent (mass: g or mg) at a constant speed (between 100 and 250 rpm) in a liquid solution (volume fixed: mL, L) at a known initial concentration (ppm, mg. L⁻¹ or mmol. L⁻¹) and following the evolution till the specified time is reached (Benettayeb et al., 2022, 2023). Generally, the concentration or the change in the concentration of the adsorbate is measured during the contact time, and the process can be continued until equilibrium is reached.

2.2. Dynamic regime (fixed bed column) adsorption

It consists of an adsorbent bed with continuous flow of liquid solution with target contaminant to be removed (Gu and Evans, 2007). Exploitations of fixed bed sorption, also called percolation, consist of both uptake of dissolved organic pollutants and inorganic contaminants from waters and wastewaters. An expanded contacting with feed fluid will eventually bring about eliciting a thermodynamic equilibrium between the solid sorbent support and fluid phase. It is an unsteady state rate-controlled process, which implies that circumstances at any particular locale inside the fixed bed are varying with time.

3. Comparison of batch and column modes

3.1. Batch mode (discontinuous adsorption)

Batch adsorption is used to obtain data and parameters on the removal of adsorbates like equilibrium adsorption isotherms and to assess the adsorption capacity of adsorbents. Thus, batch mode experiments are performed in conical flasks, beaker or glass flask and stopper with known volume and contaminant concentration. This flask or beaker is chosen based on the volume treated, the treatment time, the stirring

speed, and the type of agitator. A given mass of the sorbent (g), which could be in the form of powder, beads, fibre or membranes, is added to a solution of known volume V (mL). The beaker is stirred at constant speed (between 100 and 250 rpm) for a sufficient contact time (t_{eq}) until equilibrium reached, on a shaker incubator at room temperature (or at a temperature chosen by researchers) to simulate environmental conditions.

For kinetic studies, samples are collected at prespecified time intervals to analyse residual level of the adsorbates remains in the solution. Usually, an atomic adsorption spectrophotometer (AAS) for metal ions and an UV-Visible spectrophotometer for dyes are used. For isotherm determination, the parameters must be optimized first and the equilibrium time is used to determine the sorption capacity at different equilibrium concentrations.

3.2. Dynamic column mode (fixed bed or continuous pack bed adsorption)

A fixed-bed column research can be performed in several manners, but generally follow similar methodologies. Fixed bed columns have vertical tubes of a certain height ($Z_1, Z_2, \dots$) and diameter ($D_1, D_2, \dots$), which are filled with bio-adsorbents. The system proceeds by unsteady rate-controlled processes. In a fixed bed column, a feed is pumped from the top (or bottom) of the column, which is filled with biosorbents. As the stream passes through biosorbents in the column, the contaminants are adsorbed from mobile phase and the purified mobile phase exits the column (Malik et al., 2018a). The effluent can either be evacuated directly, or pass through an additional acid/base treatment to ensure its neutrality (see Fig. 2).

The upstream and downstream movements of the effluent in the column bed can be controlled to insure a defined flow rate (mL/min) (Malik et al., 2018b). To determine the adsorption efficiency in the columns, it is essential to analyse breakthrough curves. It is conducted by computing breakthrough curves parameters: volume at the breakthrough time (V_b) and breakthrough time (t_b) which are respectively determined as the volume and time when the outlet pollutant concentration (C_t) reaches a pre-specified percentage. According to (Nguyen et al., 2015), outlet concentration (C_t) is usually taken as 10% of the initial (inlet) concentration ($C_t/C_0 = 0.1$). Isotherms of the column mode can be calculated from Equation (1).

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad \text{Equation 1}$$

where q_{total} is total amount adsorbed in (mg); Q is volumetric flow in mL/min; C_{ad} the concentration of adsorbate ($C_{ad} = C_0 - C_t$; mg/L); t the time (min) ; .

The maximum column capacity (q_e) is defined as total amount sorbed (q_{total}) per gram of sorbent (w) at the end of the total flow time (Equation (2)).

$$q_e = \frac{q_{total}}{W} \quad \text{Equation 2}$$

According to (Tchobanoglous and Burton, 2003) the performance of the column can be studied by computing the breakthrough time and the sorption capacity. The sorption capacity at a breakthrough of 10% was computed based upon Equation (3) (Biswas and Mishra, 2015).

$$q_B = \left(\frac{x}{m}\right)_B = \frac{x_B}{m_{adsorbent}} = Q_v \left(C_0 - \frac{C_B}{2}\right) \frac{t_B}{m_{adsorbent}} \quad \text{Equation 3}$$

where C_0 is the concentration of pollutant (mg/L); x_B is the mass of pollutant adsorbed in the column at breakthrough (mg); $m_{adsorbent}$ is the mass of adsorbent in the column (g); Q is the flow (mL/min); C_B is the breakthrough pollutant concentration (mg/L); and t_B is breakthrough time (min).

This process proceeds till the column bed is saturated, i.e., all of the sites accessible for pollutant adsorption are used, resulting in an augmentation in the concentration of targeted pollutant in the outlet effluent. Thereafter, the flow of the effluent stream is either stopped or diverted to another column bed (in the case of adsorption columns in series) where it must be recovered by regenerating solutions (acidic or basic solutions).

Utkarsh Upadhyay et al. (2021) have summarized the properties of dynamic mode of adsorption, which is commonly used in the chemical industry. This method involves pumping an effluent stream into a fixed bed column that is filled with bioadsorbents. As the stream flows through the column, the adsorbents get filled with metal ions from the stream, and the metal-free stream exits the bottom of the column. This process continues until the column bed reaches the saturation stage, which is when most of the active sites available in the adsorbent have been used, resulting in a high concentration of metal ions in the outgoing currents.

At the end of the process, the flow can either be directly rejected into

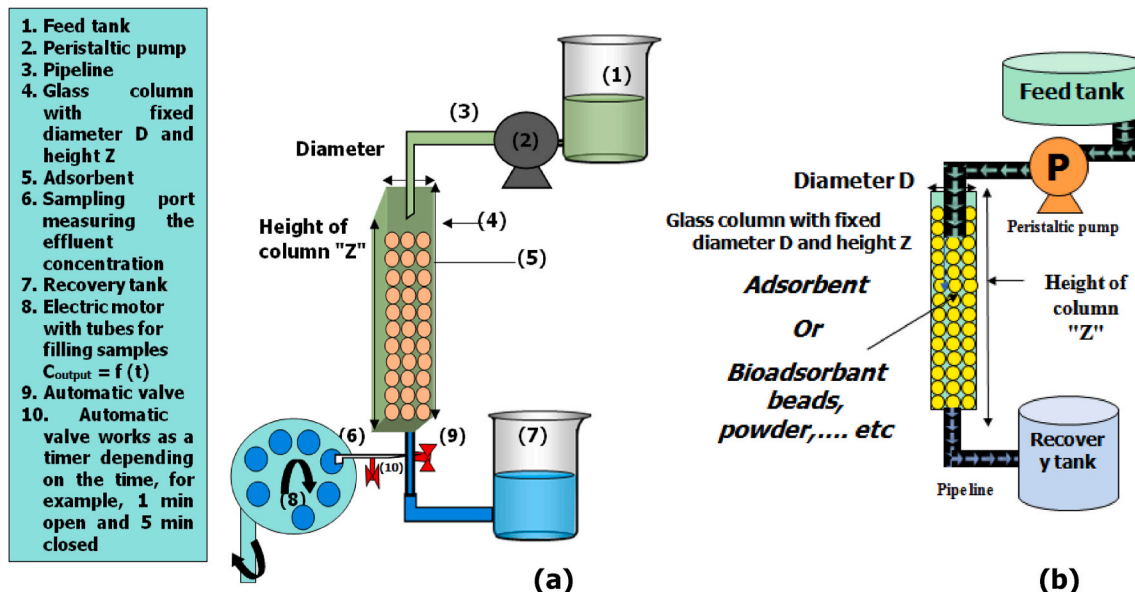


Fig. 2. Schematic of experimental set-ups for dynamic adsorption in a column ((a) and (b)).

the environment or directed to the top of the column for acid/base treatment to ensure that the pH of the flow released to nature is neutral. The flow initially directed to the fixed bed is either stopped or redirected to another column bed, where it is treated with regenerating agents (Upadhyay et al., 2021). These agents can desorb or recover pollutant particles from the surface of the adsorbent to prepare them for further use. Other researchers have proposed alternative processes (Bouzitamel, 2019; Chao et al., 2014; Oguz, 2017; Tsai et al., 2016).

3.2.1. Is batch mode sufficient to confirm the effectiveness of adsorbent X regarding pollutant Y, or is it necessary to switch to dynamic mode?

It's important to understand the two modes of adsorption when treating industrial effluents. The batch mode adsorption is the initial step before moving on to the second mode, which is the "dynamic mode". The second mode is a crucial step that is carried out on a mini-pilot laboratory scale before the actual industrial treatment takes place.

Taking into account that the X adsorbents selected in batch mode are not suitable for direct transition to industrial scale and do not meet the necessary conditions in real mode. Therefore, it is necessary to move from batch mode to dynamic continuous mode to test the effectiveness of these adsorbents under some conditions close to reality. Knowing that, continuous flow processes and in particular, fixed bed columns are the most commonly used in the treatment of industrial wastewater (Kanamarlappudi et al., 2018). And in this process the speed of the liquid introduced into the column is controlled by a peristaltic pump (Malik et al., 2018a). Several researchers in the field of adsorption suggest that batch mode adsorption experiments are simple and can provide a good understanding of adsorbent properties, kinetics, and the general mechanism of adsorption (A Benettayeb et al., 2021a, 2021b; Benettayeb et al., 2022; Guibal et al., 2002; Hamza et al., 2022a; Imam et al., 2018; Villen-Guzman et al., 2019; Wang et al., 2017). Therefore, the goal of batch mode is to choose the best adsorbent (based on its structure, synthesis, and active site) for each pollutant and optimize its operating parameters to maximize the efficiency of the adsorption process.

3.2.2. The advantages of switching to dynamic mode

The advantages of switching to dynamic mode are: (1) The adsorption in batch is exploited for small quantities of wastewaters with minimal pollution loads, while the dynamic method is suitable for large quantities of wastewaters; (2) Batch operations are not in demanded for industrial applications. This implies that dynamic mode is preferable in industry for the removal of contaminations from higher quantities of wastewater with a higher pollution load; and (3) In dynamic mode, the adsorbates are in continuous contact with a given amount of fresh adsorbent. The contact duration is not long as in batch adsorption, and upon bed saturation the adsorption process will terminate.

3.2.3. Breakthrough curves

Dynamic mode adsorption is a process where the flow rate controls the adsorption in a fixed bed. As the conditions at a specific point in the bed change with time, time is a crucial factor for the process continuity and to draw the breakthrough curve. The success of the dynamic mode adsorption process depends on the type of breakthrough curve obtained, which needs to meet international standards. Thus, getting a good breakthrough curve is essential.

So, the performances of fixed-bed columns are evaluated using breakthrough curves, which represent the pollutant-effluent concentration profile as a function of time in a fixed bed column. Breakthrough curves have an S-shaped curve with a variable slope. They provide an estimate of the maximum pollutant volume that a column bed can treat based on the maximum allowable pollutant concentration. These curves help to determine the output effluent current. Fig. 3 shows an example of a correct breakthrough curve.

The column lifetime and regeneration time can be predicted by breakthrough curve of the system. The shapes of the breakthrough curves depend upon the inlet flow rate, bed height, column diameter, initial and final concentrations of the adsorbates, and adsorbent's physico-chemical features (Hu et al., 2020b, 2020a; Liu et al. ; Zhang et al., 2019). A fixed bed of certain dimensions (height and diameter) has a defined capacity to adsorb solutes running into the bed, and the equilibrium quantity and the adsorption rate depends on the transfer

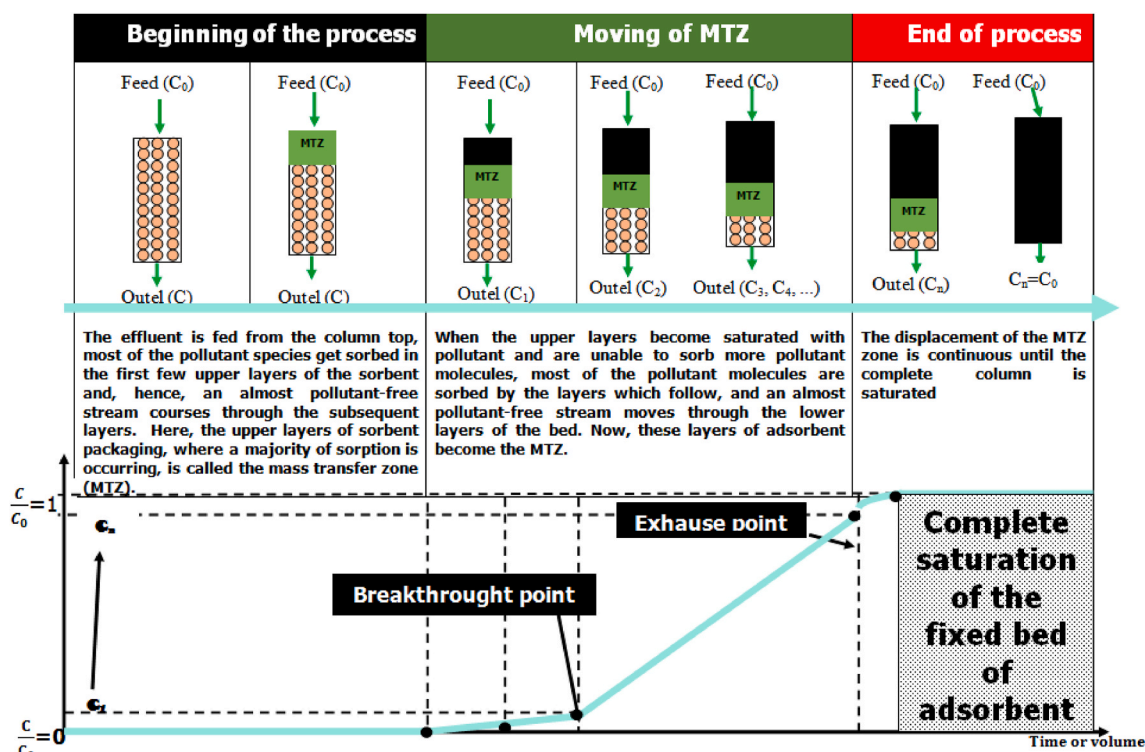


Fig. 3. Movement of mass transfer zone and related breakthrough curve.

mechanism. During operation time, adsorption actively occurs in a limited region of the bed which is known as the mass transfer zone (MTZ). As time proceeds, the MTZ starts at inlet, moves along the bed length and finally exits from the end of sorbent bed. The concentrations along the MTZ region varies from zero, ahead of MTZ, to saturation, behind the MTZ region, i.e. $C_t/C_0 = 0$ to $C_t/C_0 = 1$, and eventually the adsorbent reaches the equilibrium capacity i.e., saturated with adsorbate (Bombuwala Dewage et al., 2018; Chowdhury and Saha, 2013; Hasanazadeh et al., 2017; Patel, 2019; Shafeeyan et al., 2014).

The mass transfer zone and an instance breakthrough curve have been demonstrated in Fig. 3, in which C_0 is the starting point of the adsorption operation with an adsorbent x and an adsorbate y . At the start, the adsorbate is adsorbed quickly by the first fixed bed layer (upper layers) because of the availability of sites with respect to adsorbates (adsorbate concentration (C) is zero on the adsorbent surface. After saturation of the first layer, MTZ moves towards the next part of fixed bed containing unoccupied active sites, and the MTZ descends towards fresh layers following points C_1 , C_2 , ..., until saturation of the fixed bed ($C/C_0 = 1$) is reached. If MTZ passed, it does not return and adsorption is strongly linked to the phenomenon of mass transfer.

It's important to keep in mind that the shape of breakthrough curves is affected by various factors such as internal diffusion, external transfer, axial dispersion, and the adsorption isotherm. When the concentration profile is managed effectively, we can obtain a good breakthrough curve, indicating that the process is functioning properly. A good breakthrough curve is characterized by a long breakthrough time (T_b), which is the time from when the bed starts to saturate. However, many researchers in this field have obtained breakthrough curves that contain errors and defects probably for different reasons (Abir, 2016; Benallou Benzekri et al., 2018; J. Thilagan et al., 2015; Kaur et al., 2013; Lin et al., 2017; Mokhtar, 2018; Moscatello et al., 2018; Patel, 2019; Wolowicz and Hubicki, 2020; Xu et al., 2018):

The process operation is unstable and incorrect due to several reasons.

- 1 the adsorbent is deposited randomly in a non-uniform fixed bed, which leads to a large space between the adsorbent molecules.
- 2 This causes poor liquid-solid contact resulting in the failure to obtain the $C_0/C_{eq} = 0$ ratio during the breakthrough time.
- 3 Manual valve use, variation in liquid speed along the pipe, causing a change in the liquid-solid contact speed.
- 4 uncontrolled flow during the process operation period.
- 5 poor management of sampling time, which leads to a poor breakthrough curve with voids due to disturbances during sampling.
- 6 the effectiveness of the adsorbent was not initially tested in batch mode
- 7 Also, the analysis method and errors made by the researcher himself further contribute to the problem.

3.3. Comparison of the two modes

There are several differences between adsorption in batch mode and in dynamic mode, but the idea is that adsorption in batch mode completes the dynamic study. Thus, dynamic mode cannot be attained without gathering data from batch mode at the first stage of studying the adsorption system. Batch adsorption is used to obtain imperative data and parameters on removal of adsorbates like adsorption isotherms, and adsorption capacity of an adsorbent. Column adsorption provides information on adsorption study of various types of adsorbents and this information is useful for filtering adsorbents, which meet conditions for industrial application (Vijayaraghavan and Balasubramanian, 2015). The continuous or dynamic operating mode is vastly exploited with both gases and liquids feed. Adsorption only occurs in a special region of the bed, the MTZ, which moves along the bed. The advantages of fixed bed over batch systems are simplicity of equipment needed, the capability of being upscaled for industrial use and relatively cheap to be construct

and investigate.

Fixed bed systems, however, have drawbacks too. As the adsorbate solution is run into the fixed bed of solid supports, transfer of species from solution to the solid initially occurs at the bed entrance. Then, until the sorbent in the entrance gets fully saturated with the sorbate (breakthrough point), the MTZ progressively moves through the bed. Also, there is a discontinuity within the column, where sorbent beads downstream or upstream of MTZ do not contribute in mass transferring processes at a given time. In order to compensate this discontinuity, it is essential to exploit multiple columns of adsorbent in the system.

Batch adsorption is favoured at laboratory scale to predict performance of adsorbents before applications in large industrial scale. Only small amounts of materials are employed and is less time consuming. Batch adsorption is convenient for small scales studies but not desirable for industrial applications.

Adsorptions in columns have more advantages over batch-type operations, because in batch operations, the adsorbent's performance in removal of an adsorbate from the solution declines as the adsorption progresses. Whilst in column mode, adsorbent is continuously in contact with a fresh solution and, as a result, the adsorbate concentration in the solution which is in contact with adsorbent, at a given point in the column is relatively constant. Columns are easy to operate, faster and easily up-scaled to industrial processes (Patel, 2018, 2019). The contact time exploited in the batch operation is not enough for equilibrium attaining in a column. It is important to note that the concept of equilibrium in adsorption during batch processing is different from that in dynamic mode. Equilibrium is achieved when the concentration of the adsorbate in the liquid phase remains constant. The time it takes to reach equilibrium in dynamic mode is influenced by various factors, such as the solubility of the adsorbate, pH, temperature, concentration and composition of the pollutant, and the nature of the adsorbent (specific surface area and porosity). To obtain a good breakthrough curve, we need to consider three points: (1) adsorption equilibrium, (2) adsorption kinetics, and (3) fixed bed hydrodynamic parameters.

Thus, further optimizations of column circumstances after optimizing the parameters in batch mode (m , V , t , T , etc.) are necessary to be able to design the column set-up. Outcomes withdrawn from batch investigation cannot accurately predict up-scale to column adsorption, because of less contact times, but can still predict the performances (Vijayaraghavan and Balasubramanian, 2015).

In most cases, a bioadsorbent used successfully in laboratory batch experiments may not be successful in treating industrial effluents for several reasons. Industrial effluents have much more complicated matrices than aqueous phases tested in laboratory. Organic species, metal ions, anions and heavy metals in industrial effluent all compete for active sites on biosorbents, with an overall decrease in heavy metal removal efficiency (Sazali et al., 2020). Another problem, which does not arise in batch tests, is that some adsorbents tend to swell in the adsorption system. Thus, the flow of liquid into columns filled with adsorbent is blocked, resulting in failure of adsorption processes (Ali, 2014). Table 1 is a comparison of batch and dynamic modes of adsorption, which shows that fixed bed column (dynamic mode) is industrially feasible and preferable to remove wastewater contaminants.

Column and batch biosorption have more advantages than classic adsorbents because natural environmentally friendly adsorbents are used. The use of biosorbents in batch and continuous modes are summarized in Table 2 and successful studies are given for a comparison between the two modes.

4. Effects of physico-chemical factors on column adsorption

To improve fixed bed column operations, breakthrough curves are predicted by varying the initial level, pH, height, diameter, and flow velocity to achieve optimal and efficient parameters. Optimal parameters contribute to the efficiency of column mode adsorption processes. The effects of various factors on biosorption in batch and column modes

Table 1

Comparison of batch and dynamic modes of adsorption.

Batch adsorption	Column adsorption
Adsorbents and adsorbates are well agitated in diluted solutions of 0–200 mg/L, preferably at constant volumes (using mechanical or magnetic stirring)	Fixed-bed systems consist of an adsorbate which is in continuous flow through an adsorbent's bed at a fixed rate
important data on the elimination of the adsorbate is elucidated (efficiency, capacity, operating parameters in batch mode,)	Selection of the adsorbents that meet important conditions for industrial applications (best adsorbents that can pass to industrial application through the test in dynamic mode).
create a database for each adsorbent vs. each adsorbate (examine the properties of the adsorbent and their behaviour with respect to certain adsorbates, thus predicting their mechanisms)	Very easy, cheap technic, innovative and easy to modify according to the need and the effluent (quantity, composition, etc.)
Very simple and inexpensive technique, and easy to monitor the effect of all parameters	Poor temperature controller, undesirable heat gradients, and the equilibrium time is not precise
The equilibrium time and temperature and the swelling rate must be tested in batch mode	Used for higher quantities of wastewater and large volumes of contaminated effluents with maximum pollution loads
Used to analyse feasibility of sportive interactions between adsorbent and adsorbate.	Difficult to adsorb or clean compared to batch adsorption
Exploited for small quantities of wastewaters having minimal adsorbate loads with a constant V/m ratio	Reduce space and time, thus, requiring a very short contact time between the adsorbates and the adsorbents.
Contact time varies according to the adsorbent and the conditions of the adsorption operation (agitation, time, etc.)	The performances of the fixed bed column are assessed by breakthrough curve, which is a presentation of contaminant-effluent level profile as a function of time in a fixed bed column.
Kinetics and isotherms models are used study the performances of batch adsorption	The breakthrough time is decreases with an increase in particle size of the sorbent. The maximum particle size is favoured to obtain a higher sorption capacity.
The adsorption capacity increases with a decrease in an adsorbent particle size (the degree of adsorption should be proportional to the specific surface area).	Small particles cause a large pressure drop in the fixed bed column
Possibility of using several physical forms	The choice of physical form is necessary to improve the adsorption and minimizing the risk of clogging and pressure drop
Adsorption varies with availability of active site	Adsorbents must be replaced or regenerated continuously, because MTZ does not participate in the mass transfer process even if the first fixed bed layer is unsaturated Adsorption is directly linked to MTZ (Patel, 2019, 2021)

are summarized in Table 3.

4.1. Effect of pH

Xie et al., scrutinized the biosorption of Pd(II) from acidic solutions in a fixed bed column. The adsorption was modelled by the Langmuir isotherm and pseudo second order for the kinetics, with a maximum adsorption capacity of 197.23 mg/g. The authors showed that the increase in pH from 1.0 to 3.0, increased adsorption capacity of Pd(II) in solution from 41.46 mg/g to 84.32 mg/g. The increase was a result of Pd (II) metal speciation at low pH, which implied the existence of different species in the solution like $PdCl_3^-$ and $PdCl_4^{2-}$ (Xie et al., 2020). As the flow rates were increased from 3.0 to 5.0 mL/min then to 8.0 mL/min, an increase of adsorbate concentration in the effluent was noted from 3.5 mg/L to 17.59 mg/L to 21.38 mg/L, respectively. The results showed that with an increase in flow rates came a decrease in adsorption

capacity of Pd(II).

Subedi et al. (2019), as described in the work of Xie et al., studied magnetic chitosan ($Chi@Fe_3O_4$) nanocomposite for effective uptake of Cr (VI) from waters. The reaction kinetic fitted well with the pseudo-second order and Langmuir model for isotherms, with a maximal adsorption capacity of 142.32 mg/g. An increasing in pH led to a decrease of adsorption capacity of the Cr(VI) ions with the highest capacity (84.84 mg/g) obtained at pH 2. At low pH levels, there was addition of H^+ ions on the surface of the sorbent (hydronation), leading to an increase of the electrostatic attraction betwixt the adsorbate (Cr ions) and the adsorbent surface (Subedi et al., 2019; Xie et al., 2020).

Shirani et al. (2018) studied efficient removal of toxic aquatic pollutants (focusing on Cr(IV) ions) utilizing *Moringa oleifera* seed pods as adsorbents. The adsorption isotherm and kinetic results was modelled with Langmuir model and pseudo second order kinetic model, respectively (Shirani et al., 2018). At pH 1.0, the adsorption of Cr (IV) was 95% and a stepwise increase of pH from 2 to 10, led to a decrease in Cr (IV) ion removal from the solution. Therefore, pH 1 was the optimum for the biosorption. The decrease in adsorption can be explained by the existence of hydroxyl ions at higher pH levels, which results in a competition between the Cr (IV) ions and the hydroxyl ions to occupy active sites on adsorbent surface. An increasing in pH decreases the adsorption of Cr (IV) ions.

4.2. Effect of mass

Xie et al. (2020) displayed that an increasing in biosorbent mass in a fixed bed from 5 g to 10 g then 15 g resulted in a decrease of adsorbate concentration in the effluent from 15.32 to 3.32 to 0.35 g/L with an increase in depletion time from 180 to 320–360 min, respectively. These results show that an increase in biosorbent mass increases the breakthrough time and column depletion time (Xie et al., 2020). The authors confirmed that an increase in adsorbent dosage from 0.5 to 2.5 g/L resulted in an increased percentage removal of Cr (IV) from 90 to 99% for fine fraction adsorbent, 22.16% for mixed fraction adsorbent and from 52.69 to 85.85% for coarse fraction adsorbent. The increased removal of Cr(VI) by higher adsorbent doses can be a result of the increasing in surface area and accessibility of more active sites (Shirani et al., 2018).

4.3. Effects of sorbent dosage

The Subedi et al., demonstrated that an increasing in adsorbent loading from 25 to 50 mg resulted in a delay of breakthrough curve and a decreasing in adsorbate concentration in the effluent from 17.26 to 14.14 mg/L. As the sorbent dosage increases, the available adsorption sites increase and therefore more Cr ions were adsorbed (Subedi et al., 2019).

4.4. Effects of concentration

Subedi et al. (2019) found that a twofold increase of pollutant concentration in the feed resulted in an increasing of pollutant level in effluent from 17.26 to 43.82 mg/L. An increase of the influent concentration leads to early saturation of accessible adsorption sites and the rest of the unadsorbed pollutants flow out of the column in the effluent solution. When the flow speed was doubled from 1 to 2 L/min, adsorption capacity decreased, as evidenced by the increase of adsorbate concentration in the effluent from 17.26 to 21.02 mg/L. Such a tendency can be assigned to insufficient residence times because of higher inflow of contaminants solutions, leading to lesser adsorption of Cr(VI) ion (Subedi et al., 2019).

According to yunnan et al., a decrease in initial concentration causes a slower transport speed and therefore a longer contact time (Yunnan et al., 2017). Chang et al., recorded a steeper breakthrough curve when the concentration of Cs(I) increased (Chang et al., 2018). Similar results

Table 2

Adsorption results of pollutants in column and batch modes.

Material	Pollutant	pH	T (°C)	SD (g/L)	Isotherm models	Kinetic models	Q _{max} (mg/g)	Mechanisms	Column or batch	Operating conditions in mode column	Ref.
Chitosan immobilized on bentonite	Cu(II)	–	20	0.5	Freundlich And Thomas	–	14.92	–	Column	Fixed bed height (Z = 4.3 cm) Flow rate = 0.2 ml/min	(Reddy et al., 2010)
Chitosan-coated bentonite	Pb(II) Cu(II) Ni(II)	–	–	0.2	Freundlich Adams Bohart Thomas Yoon-Nelson	–	13.49 12.14 10.29	–	Column	Fixed bed height (Z = 2 cm) Flow rate (0.4 ml/min)	Wan Ngah et al. (2002)
Encapsulated <i>Moringa oleifera</i> bead (EMB) with Ca-alginate	Zn(II) Cu(II) Mn(II) Co(II) Ni(II)	–	Room temp.	–	Thomas Yoon-Nelson	–	55.5 63.1 74.5 64.9 104.5	–	Column	Flow rate = 1 ml/min Column diameter = 4.5 cm Column length = 55 cm Fixed bed height = Z: 5–25 cm	(Radhakrishnan et al., 2016)
Chitosan beads	Cu(II)	6.0	–	–	Langmuir	–	80.71	–	Batch	–	Wan Ngah et al. (2002)
Chitosan/MWCNT/Fe ₃ O ₄	Cr(VI)	2	45	0.5	Langmuir	Pseudo second order	358.0	chemisorption	Batch Column	Flow rate = 4 mL/min	Beheshti et al. (2016)
Chitosan immobilized in alginate beads	Cu(II) Cd(II)	–	–	–	Sips	–	527.3 207.0	–	Batch	–	Kebede et al. (2019)
Material	Pollutant	pH	T (°C)	SD (g/L)	Isotherm models	Kinetic models	Q _{max} (mg/g)	Mechanisms	Column or batch	Operating conditions in mode column	Ref.
<i>Moringa oleifera</i>	Cd(II)	7.5	55	0.3	Langmuir	–	–	–	Column	Flow rate = 2 ml/min	Shirani et al. (2018)
Chitosan/bentonite/MnO composite beads	Mn(II)	6	–	3.33	–	–	15.22	–	Column	Column diameter = 20 mm Column height = 300 mm Bed height = 2 cm	Muliwa et al. (2018)
Powdered <i>Moringa stenopetala</i> seed husk	Cd(II) Pb(II) Cu(II)	5	30	0.75	Freundlich	Pseudo second order	52.63 47.62 31.25	–	Batch	–	Kebede et al. (2019)
Polyaniline grafted chitosan	Pb(II) Cd(II)	6	–	–	Langmuir	–	16,07 14,33	–	Batch	–	Karthik and Meenakshi (2015)
Chemically modified <i>Moringa oleifera</i> leaves	Pb(II)	5	40	–	–	–	209.54	–	Batch	–	Reddy et al. (2010)
Chitosan modified biochar	Pb(II)	5	45	–	Langmuir	–	134 5.8	–	Batch Column	Column diameter = 1 cm Column length = 20 cm Fixed bed height = 5 cm Flow rate = 2.5 ml/min Bed height = 2 cm	(Bombuwala Dewage et al., 2018)
							119.02	–	Column		

were obtained in these studies, due to the decrease in mass transferring flux of bulk solution at the surface of adsorbent when the driving force became weaker (Baek et al., 2007; Sivakumar and Palanisamy, 2009). Breakthrough and saturation were attained more rapidly with an increasing in initial concentration of adsorbate (Cr(IV)) in the influent, implying a rapid exhaustion of the fixed bed (Shirani et al., 2018). As the adsorbate concentration increased, effected a stronger concentration gradient and a decrease of mass transferring resistance of adsorbate from solutions to the surface. A continued increase in the Cr(IV) concentration in the influent did not have a great effect on the breakthrough curves, because the available active sites for adsorption was saturated. An increasing in the adsorbate concentration results in an increase in

adsorption but only to certain limits (Shirani et al., 2018).

4.5. Effects of flow rate

The impact of flow rate on the Pd ion's adsorption can be elucidated by contact duration necessary for reaction betwixt the immobilized biosorbent and the flowing Pd(II) solutions (Xie et al., 2020). According to Taty-Costodes et al. (2005), when the flow speed declines the contact duration in columns is longer, and intra-particle diffusion becomes influential. Hence, metal ions have more times to diffuse among the beads of sorbent and higher adsorption capacities are acquired (Taty-Costodes et al., 2005).

Table 3

Summary of the effects of various factors on biosorption in batch and column modes.

	Batch mode	Column mode
Effects of temperature	Increasing in temperature increases adsorption capacity in cases of physio-chemical adsorption but decreases in cases of physio-sorption	- Increase in temperature increases or decreases adsorption with respect to the type of adsorption mechanism - Breakthrough time is slower with increasing system temperature (Girish and Ramachandra Murty, 2014; Ye et al., 2018) - Generally, adsorption sorption capacities decline with increase in temperature. This is because the high operating temperatures favouring diffusion of the adsorbate more quickly into the adsorbent, resulting in a low penetration and escape time (Patel, 2019)
Effects of sorbent dosages	Increasing in sorbent dosages increase adsorption sorption capacities	- Increase in adsorbent dosage increases adsorption capacity due to the availability of more active sites on sorbent surface - Increasing the inlet pollutant concentration reduces the volume processed before the bed becomes saturated. High concentration of pollutants saturate the adsorbent quicker, thus decreasing breakthrough time
Effects of adsorbate concentration	Increase in adsorbate concentration increases adsorption capacity	Increase in adsorbate concentration increases adsorption capacity but only to a certain level where the adsorbent gets saturated
Effects of contact time	Increase in contact time increases adsorption efficiency	Increase in flow rate decreases adsorption capacity due to lack of sufficient time between adsorbent and adsorbate (reduction in contact time betwixt contaminants and sorbent at a higher flow rate)
Effect of pH	Increase in pH decreases adsorbate removal capacity	- Increase in pH decreases adsorption capacity due to formation of other pollutant species, which compete in the process of sorption - Highest removals at acidified pHs and maximal removals of some adsorbates at alkaline pHs (Ahmed and Hameed, 2018)

Shirani et al. (2018) show that an increasing in the flow rate from 1 to 2–5 mL/min leads to steeper breakthrough curves and the biosorbent is rapidly saturated at higher flow rates. As a result, there is a decrease in adsorption of the metal onto the surface of biosorbent. This is because at a lower flow rate, there is more contact time betwixt the adsorbate and biosorbent and greater uptake is achieved (Shirani et al., 2018). According to Biswas and Mishra (2015), at a concentration of 20 mg/L, bed

height 5.0 cm and pH 5.2 with a feed rate increase by 10 ml/min till 20 ml/min, the saturation time decreases because of the occupation of active sites. Therefore, saturation of bed requires less time with increase in flow rates (Biswas and Mishra, 2015).

4.6. The effects of column length

The impact of fixed bed column length on breakthrough curves show that the breakthrough volumes vary with the depth of bed and increases with bed height (Taty-Costodes et al., 2005). According to Wang et al. (2018), at a constant flow speed of 5.0 L/min, the saturation times increase with increasing in bed heights (5 cm, 10 cm and 15 cm). This is expected, a higher column has more sites accessible for adsorption and will need more times for bed saturation. In addition, $q_{\max}$ was 0.538, 0.501 and 0.468 mmol g⁻¹ for heights of 5, 10, 15 cm, respectively (Wang et al., 2018). Such a declines in adsorption capacities with column heights may be because of the effect of liquid channelling and poor distribution of the adsorbent in the bed (Muhamad et al., 2010). The same behaviour was observed when the influence of bed depth on the breakthrough curve at a fixed flow rate of 15.0 ml/min, pH 5.2 and concentration 20.0 mg/L was studied (Biswas and Mishra, 2015).

5. Thermodynamic study in batch and column mode

Temperature is also considered as an important factor to determine the nature of adsorption (chemisorption or/and physio-sorption) in static or even dynamic mode and one can estimates the feasibility of the process with thermodynamic parameters. The parameters are developed under the assumption that the distribution of adsorbate was uniform across the surface of sorbent (Belala et al., 2011). The adsorption process is a reversible process characterized by a thermodynamic equilibrium between the solute in solution and that adsorbed on the surface of the solid. An increasing in temperature leads to a decline in adsorption capacity, when adsorption is exothermic, and it is other way round when the process is endothermic (Sahel and Ferrandon-Dusart, 2005).

Badessa et al., conducted isotherm experiments with initial metal ion concentrations betwixt 10 and 500 mg/L at pH 5.5 at three temperatures (25, 35, and 45 °C) and an adsorbent concentration of 1 g/L. An increase in the adsorption capacity was observed with an increase in temperature.

Thus, a decline in Cr(IV) removal percentage from 91.40 to 37.93% from the solution containing *Moringa stenopetala* seed powder (MSSP) as observed (increased $q_{\max}$ from 1.37 to 0.57 mg/g) as temperature increased from 293 to 353 K. Such falls in ad/sorbent pollutants removal capacities with increasing temperature may be because of desorption occurred by increasing in accessible thermal energy. Declines in adsorption capacities with increases in temperatures indicate that the adsorption processes are exothermic in nature (Badessa et al., 2020).

Hefni et al., studied the impact of temperatures upon the adsorption process at three temperatures (22, 30 and 40 °C) with metal concentrations of 5.4 mg/L Mn²⁺, 2.33 mg/L Pb²⁺ and 24.2 mg/L Al³⁺ (Hefni et al., 2020). The results show that increase in temperature of solution increases the mobility of pollutant (metal ion) and causes a swelling influence within the internal structures of Chitosan and its derivatives, hence enabling large metal species to diffuse further. Temperature also is influential on the adsorption rates by changing molecular interactions and solubility. Greater uptake of Mn²⁺, and Al³⁺ at higher temperatures might be assigned to the chemical reaction occurring betwixt functional moieties of sorbent and the sorbate molecules, whilst the decline in Pb²⁺ uptake is because of physisorption.

Thermodynamic studies of the adsorption of Pb(II) by immobilized *Providencia vermicola*, noted a negative value for ΔG^0 , which indicated the feasibility of biosorption. The positive value for ΔH^0 indicated that the biosorption was endothermic; therefore, an increase in temperature increased the adsorption capacity. It was endothermic because the

biosorption involved chemical reactions of the Pd ions with the surface of the adsorbent (Xie et al., 2020). The thermodynamic studies of Subedi et al., showed that the process was endothermic ($+\Delta H^\circ$). This was due to the formation of a monolayer during the adsorption, confirmed by the fitting of isotherm data on the Langmuir model, therefore predicting that it was chemical adsorption. An increase in temperature resulted in an increase in the adsorption of the Cr(VI) ions (Subedi et al., 2019).

A constant of equilibrium betwixt sorbent and sorbate concentration in aqueous phase usually is dubbed as distribution constant (K_D) which is given in Equation (4) (Belala et al., 2011; Huang et al., 2014):

$$K_D = \frac{C_a}{C_e} \quad \text{Equation 4}$$

Where C_a is the equilibrium concentrations of adsorbate on the sorbent (mg/g); and C_e is the equilibrium concentrations in the solutions (mg/L).

Unfortunately, the above constant is not a suitable thermodynamic constant, since it has a dimension (as L/g) and is also altered by altering the initial concentration of the adsorbates. However, mistakenly, in many studies, the thermodynamic parameters are determined from the equilibrium distribution (K_D). If calculated correctly, the change in Gibbs free energy (ΔG) informs us whether the adsorption is a spontaneous or non-spontaneous process. But many studies have deduced wrong values from Equation (5) (Belala et al., 2011; Huang et al., 2014), which has been written with the form of Van't Hoff equation:

$$\ln(K_D) = -\frac{\Delta G}{RT} \rightarrow \Delta G = -RT \ln(K_D) \quad \text{Equation 5}$$

Where ΔG is the variation of the Gibbs free energy ($\text{J}\cdot\text{mol}^{-1}$); R is the ideal gases constant ($R = 8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1}$); and T is the temperature of the solution (K).

The free energy change (ΔG°) is related to the change in enthalpy (ΔH°) and the change in entropy (ΔS°), Equation (6):

$$\Delta G = \Delta H - T \cdot \Delta S \quad \text{Equation 6}$$

As a result of propagation of using incorrect constant for thermodynamic calculations, Equation (7) has also mistakenly obtained from equations (5) and (6), and has been used by many researchers:

$$\ln(K_D) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{Equation 7}$$

When the researcher exploited the variation of $\ln(K_D)$ as a function of $(1/T)$ leads to the values of ΔH° and ΔS° . Again, if calculated correctly, enthalpy informs researchers about the exothermicity or endothermicity of the adsorption process. In addition, entropy informs them about the degree of disorder at the solid-liquid interfaces, and therefore about the interactions betwixt the solute and the functional moieties at the surface of the solid.

However, as mentioned in the above, many researchers calculate thermodynamic parameters for adsorption systems without of considering physical-chemistry concepts of equilibrium (Lima et al., 2019; Rout et al., 2023).

In fact, to be exploited in the Van't Hoff relation, a correct dimensionless equilibrium constant must be withdrawn from the adsorption studies (Lima et al., 2019; Mohammadzadeh et al., 2023).

Unfortunately, in addition to K_D , many authors have utilized wrong constants, like K_c , which have dimension and cannot be used for thermodynamic calculations at all (Lima et al., 2019; Rout et al., 2023). On the other hand, some researchers have tried to simply adjust the units and obtain a wrong dimensionless constant like K_0 (Lima et al., 2019).

The errors elicited in thermodynamic parameters from utilizing flawed constants have been inspected by Lima et al., (2019). Also, with some examples, the same authors have illustrated that the most correct and convenient way for calculation of changes in ΔH° , ΔG° , and ΔS° is obtaining the right dimensionless thermodynamic equilibrium constant (K_{eq}^0) from isothermal studies and exploiting Vant Hoff equation. For

instance, for adsorption systems obeying the Langmuir isotherm, the K_{eq}^0 value (dimensionless) is numerically identical to Langmuir constant (K_L) computed in L/mol (Lima et al., 2019; Rahmani-Sani et al., 2020).

6. Isotherm models in batch and column modes

The derivation and application of isotherm models in adsorption is important because they can provide information on type and the mechanisms of adsorption processes like ion exchange, physical adsorption, and chemical sorption. These are vital requisites for the design of adsorption processes (Wang and Guo, 2020). Numerous mathematical models have been developed to represent the relationship between $q_{\max}$ vs. C_{eq} . There are different isotherm models that specifically represent experimental results in dynamic (column) and static (batch) sorption. Fig. 4 represents some illustration of possibility of adsorption mechanisms according to the model appropriate to experimental conditions.

6.1. Static mode adsorption

The most vastly utilized models are Langmuir, Freundlich, Temkin, and Sips isotherms. These models are suitably applied for single-layer adsorption. Brunauer, Emmett and Teller (B.E.T) isotherms are better suited for multi-layered adsorption, and Freundlich isotherm can also be used in multi-layer adsorption.

Fig. 4 represents the different types of adsorption isotherms. Type I isotherm is characterized by a fast augmentation in the amounts adsorbed at low equilibrium region, followed by a plateau of saturation at high concentrations. The adsorbed quantity corresponding to the plateau is the quantity necessary to form a complete mono molecular layer on the surface of the solid. For type II isotherms, multilayer adsorption begins at higher concentrations and monolayer at low concentrations. This adsorption is mixed physical and chemical. Finally, Type III isotherm shows weak adsorption at low concentrations and is linked to a movement of the adsorbent wetting by the adsorbate and infinite adsorption at high concentrations. Table 4 summarizes the details of the isotherm models.

6.2. Dynamic adsorption in a column

In dynamic adsorption, adsorbate solutions are in continuous contact with the sorbents packed in a fixed bed column. For better understanding of process, estimation of adsorption behaviour in a dynamic column is essential to predict performance, to design and optimize operating conditions (W. Kast). The sizing of column adsorption units is based upon hydrodynamic and physicochemical considerations, fluid flow rate, residence time, concentration, adsorbent affinity, and particle size.

To describe adsorption of adsorbate in liquid phase running into sorbent bed, transferring relationships betwixt the fluid (liquid) and solid (fixed) phases are utilized. For this, the profile of the concentration in the two phases must be known, as a function of time. The operating conditions for the column dynamic adsorption must be adjusted, namely uniform bed, volume flow speed, uniform concentration for the liquid phase, no phase change, negligible adsorption energy, and absence of interaction betwixt the adsorbed molecules. In dynamic adsorption, the prediction breakthrough curves are used to design continuous adsorption systems. A breakthrough curve in adsorption is the course of the effluent's adsorptive concentration at the outlet of a fixed bed adsorber (Chen et al., 2012). Table 5 summarizes the details of the isotherm models.

(a) Bohart and Adams model

According to researchers (Biswas and Mishra, 2015; Chen et al., 2012; Lee et al., 2015; Saadi et al., 2013), Bohart and Adams (1920)

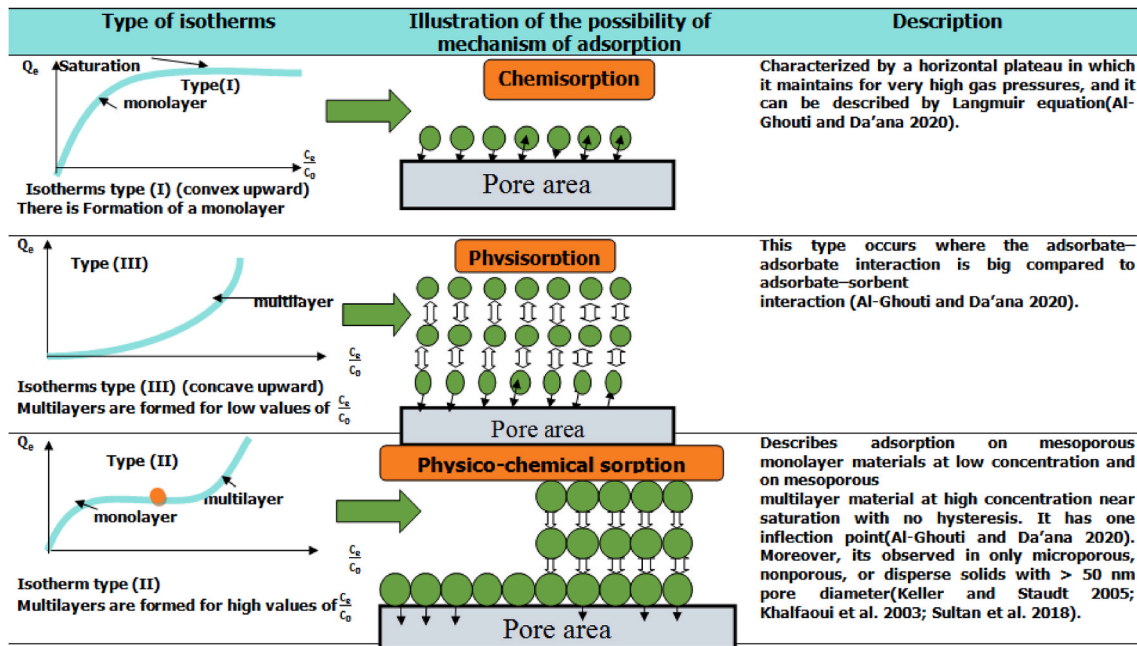


Fig. 4. Adsorption mechanism showing type of adsorption in monolayer, multilayer and possibly two types of adsorption (two-stage adsorption).

established a fundamental equation, which elucidate the relationship between C_t/C_0 and t in a continuous systems. The model postulates that the equilibrium is not instantaneous and that the rate of adsorption is controlled by an external mass transference. This model is suitable for analysing the initial parts of the breakthrough curve. The equation of Adams-Bohart model is given in Equation (8):

$$\ln \left(\frac{C_t}{C_0} \right) = K_{AB} \cdot C_0 \cdot t - K_{AB} \cdot N_0 \cdot \frac{Z}{U} \quad \text{Equation 8}$$

Where t is breakthrough time (min); C_0 the initial concentration (mg L^{-1}); C_t is the concentration at time t (mg L^{-1}); U is the speed in the reactor assumed to be empty (cm min^{-1}); N_0 is the maximum adsorption capacity (mg L^{-1}); Z is the column height with fixed bed (cm); and K_{AB} is the Adams-Bohart constant ($\text{L mg}^{-1} \text{min}^{-1}$). $\ln (C_t/C_0)$ is plotted as a function of time (t) and the line obtained is of the form $y = ax + b$. From this line, the K_{AB} parameters and the maximum adsorption capacity N_0 is derived (Nguyen et al., 2015).

(b) Thomas model or Bed-Depth Service-Time model

The Thomas model can be linearized and transformed to Equation 9, and is based upon the assumption that sorption is not restricted by chemical interactions but by mass transference at the interface, The experimental outcomes obey second-order kinetics and Langmuir isotherms (Foo and Hameed, 2010). Unlike Adams-Bohart model, Thomas model is suitable for demonstrating the entire range of breakthrough curves (Kausar et al., 2017).

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{K_{th} \cdot q_0 \cdot W}{Q} - K_{th} \cdot C_0 \cdot t \quad \text{Equation 9}$$

Where q_0 is the maximal adsorption capacity of the adsorbate on the sorbent (mg g^{-1}); Q is the column solution feed rate (ml min^{-1}); t is breakthrough time relative to the concentration C_t at the outlet of column (min); C_0 is the initial concentration of the pollutant (mg L^{-1}); C_t is the concentration of effluent at time (t) at the outlet of the column (mg L^{-1}); W is the mass of the bed (g); K_{th} is the Thomas constant ($\text{ml mg}^{-1} \text{min}^{-1}$). By plotting the curve $\ln (C_0/C_t - 1)$ as a function of time (t), parameters of Thomas' model are deduced, namely the constants K_{th} and q_0 (Kausar et al., 2017).

(c) Clark model

This model is also vastly utilized to describe processes of fixed bed adsorption. The Clark model uses the concept of mass transfer as well as the Freundlich relation for the equilibrium parameters (Han et al., 2009). The model is represented by Equation (10).

$$\left(\frac{C}{C_0} \right)^{(1-n)} - 1 = A \exp^{-r \cdot t} \quad \text{Equation 10}$$

With A (Equation (11)):

$$A = \exp \left(\frac{K_c \cdot N_0 \cdot Z}{U} \right) \text{ and } r = K_c \cdot C_0 \quad \text{Equation 11}$$

Where K_c is Clark's kinetic constant ($\text{L mg}^{-1} \text{min}^{-1}$); N_0 is the maximum volumetric absorption capacity (mg/L); C is the concentration of the solute at equilibrium (mg/L); C_0 is the initial concentration of the solute in solution (mg/L); U is the migration speed (cm min^{-1}); and Z the height of the adsorbent bed (cm). The linearization of Equation (11) gives Equation (12).

$$\ln \left[\left(\frac{C}{C_0} \right)^{(1-n)} - 1 \right] = \ln A - r \cdot t \quad \text{Equation 12}$$

The plot of $\ln \left[\left(\frac{C}{C_0} \right)^{(1-n)} - 1 \right]$ as a function of t is a line with an equation of the form $y = ax + b$ from which the parameters r and A from the slope and the y-intercept are derived (Sahel and Ferrandon-Dusart, 2005).

7. Conclusion

There are several methods to remove pollutants from water and wastewater, among them, is adsorption either in batch or column mode. Given the importance of this operation and its efficiency with regard to heavy and radioactive metals, this review gives details on adsorption in batch and dynamic mode, their efficiency, operating parameters, and the main isothermal and kinetic models. Adsorption in batch mode is carried out by most researchers by varying operating parameters like C_0 , pH, T , t , and SD. Studies on fixed bed columns are limited and still at a preliminary stage. Despite this scarcity, researchers are confident that

Table 4
Isotherm models in batch mode.

Isotherms	Linear equations	Description	Ref.
Langmuir, two parameter models	$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m}$ Plotting the curve $(1/q_e)$ as a function of $(1/C_e)$,	• Adsorption sites of the adsorbent are identical and considered homogeneous • Adsorbent sites are immobile • No interactions of the adsorbents • Formation of monolayer on the surface of adsorbent • A reaction occurs betwixt adsorbate and a vacant site of sorbent, leading to the formation of a site occupied by adsorbate	(Holik et al., 2013; Kecili and Hussain, 2018; Sensors, 1964; Largitte and Pasquier, 2016)
Freundlich, two parameter models	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$ Plotting the curve $(\ln q_e)$ as a function of $(\ln C_e)$,	• Formation of multilayers • Interactions of the adsorbents • Heterogeneous adsorption of molecules. • Applicable at low adsorbate concentration • $0.1 < n < 0.5$ characteristic of good adsorption, or $n > 1$ is weak adsorption. • The constant "n" is often replaced by "1/n" or heterogeneity factor. This constant gives information about the shape of the curve • $1/n = 1$: linear isothermal type C; $1/n > 1$: S-type concave isotherm; $1/n < 1$: L-type convex isothermal; $1/n \ll 1$: isothermal type H	(de Sá et al., 2017; Ladshaw et al., 2015; Singh, 2016) Hanane (2019)
Sips, three parameter models	$\beta_S \ln C_e = -\ln\left(\frac{K_s}{q_e}\right) + \ln(\alpha_s)$ Plotting the curve $(\ln C_e)$ as a function of $(\ln\left(\frac{K_s}{q_e}\right))$	• A combination of Langmuir and Freundlich models. At low adsorbate concentrations, this model is reduced to the Freundlich model, and at high adsorbate concentrations, it predicts the Langmuir model (monolayer adsorption) • Predicts adsorption of heterogeneous systems even at high adsorbate concentration • Possibility of presence of mixed surface and multilayer adsorption	(Tzabar and ter Brake, 2016)
Temkin	$\theta = \frac{RT}{\Delta Q} \ln K_T + \frac{RT}{\Delta Q} \ln C_e$ Plotting the curve $(q_e/q_{\max})$ as a function of $(\ln C_e)$	• For most of the time the modelling is nonlinear • Adsorption heat decreases with increase in the coverage of adsorbed molecules layers • Interactions of the adsorbates • This model makes it possible to estimate the impact of temperature and to calculate thermodynamic parameters. Only valid for an intermediate concentration range	(Foo and Hameed, 2010; Hamdaoui and Naffrechoux, 2007; Shahbeig et al., 2013)

column adsorption is better than batch adsorption, easy, simple, economical and feasible for the removal of industrial contaminants, which can lead to efficient adsorption on an industrial scale. Many parameters influence adsorption efficiency and breakthrough curves, including diameter, bed height, and flow rate. Thus, in dynamic adsorption, an adsorbent that is independent of pH, and temperature should be developed, because monitoring pH in industrial effluents is difficult and consumes time and money. The cost of exchanging the bed is expensive, and examination of literature shows little work has been done on regeneration and desorption. This cost limits application of biosorbent industrially. Therefore, it is necessary to vary this process according to the contaminant and to fabricate adsorbents that meet the need. According to researchers, a process has been developed that is effective for treating metal contaminants. However, for practical

application in the chemical industry, an intermediate step is necessary between batch and practical dynamic modes (Fig. 5). This step is called the mini-pilot scale, which helps to determine the operating parameters and the volume of effluent that corresponds to each quantity of adsorbent. During dynamic mode, several parameters such as the height of the bed, the flow rate provided by the pump, and the initial ion concentration directly influence the efficiency of the process. To address this, effluent samples are taken at regular intervals for deeper analysis. Therefore, there is a need to control the time of this process using automated methods to obtain precise results and plot these points correctly in the form of a breakthrough curve.

Table 5
The most used Isotherm models in column mode.

Isotherms	Linear equations	Description	Important parameters of model	Ref.
Bohart and Adams	$\ln\left(\frac{C_t}{C_0}\right) = K_{AB} \cdot C_0 \cdot t - K_{AB} \cdot N_0$ $\frac{Z}{U}$ Plotting the curve $\ln(C_0/C_t)$ as a function of time (t)	• Applicable for weak adsorbate concentration, only utilized for describing initial parts of breakthrough curves • External mass transfer limits adsorption speed • The adsorption rate depends upon residual capacity of the adsorbent • Equilibrium adsorbent capacity is independent of the adsorbate concentration	• k_{AB} (1/mg·min) N_0 (mg/L)	(Biswas and Mishra, 2015; Ghribi and Chlendi, 2011; Lee et al., 2015; Saadi et al., 2013; Thurgood, 2008)
Thomas	$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{th} \cdot q_0 \cdot m}{Q} - K_{th} \cdot C_0 \cdot t$ Plotting the curve $\ln(C_0/C_t - 1)$ as a function of time (t)	• Assumes Langmuir kinetics of adsorption/desorption • Obeys second order kinetics of the reversible reaction	• k_{TH} (ml/mg min)	(Abdolali et al., 2017; Biswas and Mishra, 2015; Lee et al., 2015; Malkoc and Nuhoglu, 2006; Saadi et al., 2013; Thomas, 1943; Vijayaraghavan et al., 2005)
Clark	$\frac{C_t}{C_0} = \frac{1}{(1 + A e^{-\pi})^{1/(n-1)}}$ Plotting the curve $\ln\left[\left(\frac{C}{C_0}\right)^{1-n} - 1\right]$ as a function of t	• Based upon the usage of a mass transference concept combined with Freundlich isotherm • Based on piston type flow • Used for different conditions because of good performance	• A cst	(Biswas and Mishra, 2015; Clark, 1987; Ghribi and Chlendi, 2011; Lee et al., 2015)

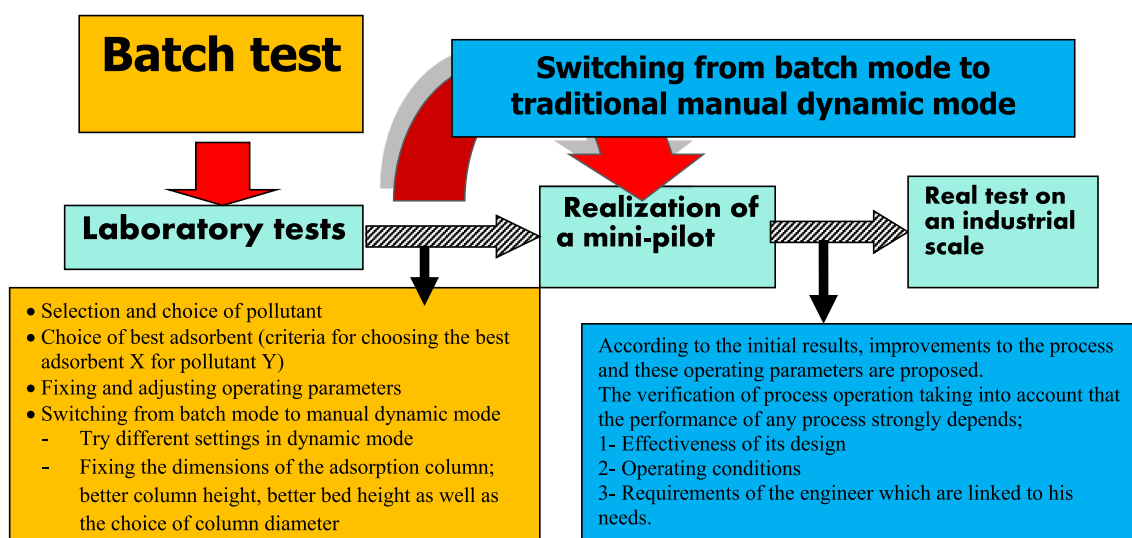


Fig. 5. Steps followed to improve the adsorption process for treating real effluent Y using adsorbent.

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CRedit authorship contribution statement

Masamvu Malbenia John: Writing – original draft, Software, Data curation, Conceptualization. **Asmaa Benettayeb:** Writing – original draft, Software, Data curation, Conceptualization. **Mohamed Belkacem:** Writing – original draft, Software, Data curation, Conceptualization. **Chitepo Ruvimbo Mitchel:** Writing – original draft, Software, Data curation, Conceptualization. **Mustapha Hadj Brahimi:** Writing – original draft, Software, Data curation, Conceptualization. **Imene Benettayeb:** Writing – original draft, Software, Data curation, Conceptualization. **Boumediene Haddou:** Writing – original draft, Software, Data curation, Conceptualization. **Saleh Al-Farraj:** Writing – review & editing, Validation. **Abdullah Ali Alkahtane:** Writing – review & editing, Validation. **Soumya Ghosh:** Writing – original draft, Software, Data curation, Conceptualization. **C.H. Chia:** Writing – review & editing, Validation. **Mika Sillanpaa:** Writing – review & editing, Validation. **Omirsrik Baigenzhenov:** Writing – review & editing, Validation. **Ahmad Hosseini-Bandegharai:** Writing – review & editing, Validation.

Declaration of competing interest

There are no competing interests to be declared by the authors.

Data availability

No data was used for the research described in the article.

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