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A Review on Batch and Column Adsorption of Various Adsorbent Towards the Removal of Heavy Metal

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ABSTRACT

The batch adsorption and column adsorption performance of various adsorbent towards the removal of heavy metal are critically reviewed. Fundamental ideas of adsorption, including chemical adsorption and physical adsorption and its component, adsorbents, and adsorbates, are incorporated. The adsorption study using various adsorbates, i.e., heavy metal (Cr, Cd, Pb, Ni, and Cu), are inspected. A set of various design experiment for batch and column adsorption are discussed deeply for removal of heavy metal. Differentiation between batch and column adsorption study are referenced. This paper explains deeply on clarification of different parameters, in both batch and column adsorption. The various parameter for column adsorption, i.e., inlet ion concentration, flow rate, bed height and for batch adsorption, i.e., contact time, pH, temperature, and adsorbent dose, are completely covered. The isotherm model, and kinetic model for both adsorptions are well described. Besides, a breakthrough curve for designing the column adsorption is completely observed. In the end, some difficulties for adaptation both adsorption in the real world are revealed.

Keywords:

Column adsorption; Batch adsorption;

Adsorbent; Heavy metal

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1. Introduction

Adsorption is a technique for separating substances from gas or liquid phase onto surface of adsorbent [1]. This is one of the method for selective separation mechanisms in which it adsorbs one or more components from the mixture on a surface. Materials used to adsorb components are called as adsorbent while adsorbate is the component that being adsorbed. Adsorbent can be classified as synthetic adsorbent, natural adsorbent and semi-synthetic adsorbent. Synthetic adsorbent is most popular adsorbent used for researcher because of high adsorption capacities but, highly in cost production. Natural adsorbent such as plant, flower and leaf give very low cost production but also give low adsorption capacity. While the semi-synthetic adsorbent that can be define as natural material combining with chemical that possess high adsorption capacity and low cost compared to

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synthetic adsorbent. In adsorption, it can be categorized as physical adsorption and chemical adsorption, where it is classified according to the bonding forces between the adsorbent and adsorbate. Physical adsorption is happening due to the attraction force of weak Van der Waal while chemical sorption happens due to the chemical bonding between adsorbate and adsorbent. When there is concentration difference between adsorbate and adsorbent, the adsorbate molecules in solution move and bind onto surface of adsorbate. To simplify, adsorption involves bonding of molecules between adsorbent and adsorbate. Generally, most solid have adsorbent characteristics but the performance of adsorption differs according to their functional groups. Currently, adsorption technology is adopted in treating textile effluents which contains several mixtures of dyes and heavy metals.

There is common adsorbent have been extensively studied and commercialized such as silica gel, activated alumina and activated carbon. Activated carbon is the main adsorbent that are used for the water treatment [2]. Researchers came out with idea of using activated carbon due to its simplicity and ability to remove broad ranges of pollutants with lower cost [3]. Not limited to small scale focus, researchers also conducted study on activated carbon usage for waste streams purification. Materials for activated carbon usually have a high percentage of carbon and the adsorption capacity varies depending on their porous structure [4]. In addition, it should be noted that characteristics of carbon precursor and techniques during synthesis including the experimental condition have significant effect to the final pore size distribution for activated carbon [5,6]. This also led to varying adsorption performance. Besides activated carbon, widely increasing studies on adsorbent has produced many types of adsorbent, developed to eliminate heavy metals from effluents. The various adsorbent study is sawdust [7], carbon aero gel [8], herbaceous peat [9], fly ash [10], modified clay [11], activated carbon-zeolite composite [12] and many more [13-20]. Modifications to the surface of adsorbent was done depending on particle that is going to pass through. These modifications such as graft co-polymerization helps to enhance properties of adsorbent by modifying the physical structure and addition of new functional groups to the adsorbent molecules. This helps to increase the ability of the adsorbent to attract dye having anionic properties [21]. The use of zeolite as an adsorbent also increasingly widespread equivalent to other adsorbent. Zeolite is known as crystalline compound consist of alumino-silicates. It has uniform cavities and excellent ion exchange capacity. Zeolites remove heavy metals through two mechanisms; adsorption and ion exchange [22,23]. Substitution of alumina molecules for silicon produce negative charge density, which is good to attract cations heavy metal. The presence of metal ions in zeolite framework helps to balance the charges. Due to their superior features, zeolite is studied for utilization in several applications [24,25]. Some uses clinoptilolite in their studies to eliminate metals such as aluminium, copper and zinc from copper mine effluents. Ion exchange method is different from adsorption. For ion exchange mechanism in removal of heavy metals, exchange process between sodium ions and zeolite (Zeolite NaX) with different types of metal ions are widely investigated. The process performance of is affected by Zeolites' pore opening and equilibrium exchange between the solution and Zeolite NaX [26,27].

Heavy metals are classified as non-biodegradable component [28, 29]. Presence of heavy metals in water threaten the living organisms as it can cause health issues to not only plants but also humans and animals [30]. Most common heavy metal found in drinking water and waste water is Lead (Pb). Some health hazards possessed by Pb if consumed unnecessarily are mental retardation, decrease in amount of blood haemoglobin and causing damage to nervous system. Industrial waste water contains numerous mixtures of both inorganic and organic chemicals which complicates the treatment procedure.

Batch adsorption studies give an important data and parameter on the removal of adsorbate, while column adsorption provide information on adsorption study with different of adsorbent used

[31,32]. The small-scale experiment from the batch study can give the important information on the parameter used for adapted in industry scale by fixed bed column [33,34]. In comparison to batch adsorption, continuous column is more advantageous as it is easy to operate, faster adsorption process and simplicity of scale up process [35]. However, batch adsorption is favoured by researchers at laboratory scale investigation as only small amount of material is used and it is less time consuming. Nevertheless, batch adsorption is convenient for small scale study but not suitable for real scale application. Study of adsorption by equilibrium in batch mode enable the prediction performance of adsorbent before application in larger scale. To add, the equilibrium study also provides critical information about the efficacy of particular adsorbate-adsorbent system [36]. In column adsorption, the contact time is not long as in batch adsorption and thus, equilibrium is not reach for certain adsorption. It can be said that results from batch studies might not accurate for scale up column adsorption due to less contact time but still applicable for predicting the performance [37]. Therefore, it is crucial to check the practicality of adsorbent in continuous mode.

Fixed bed adsorption is widely utilized to purify liquid mixture including mixture from industrial waste water [38]. Recently, this method is studied for a large-scale removal of heavy metal effluents [39]. To calculate and predict the performance of adsorption, mathematical model has been developed and used to estimate the breakthrough curves. Also, the mathematical equation is employed in current removal of organic pollutant from waste water [40]. Two information that are required in order to design an adsorption fixed bed is its dynamics and rate data [41]. Consideration that need to be taken is the influence of operating parameters on the adsorption by fixed bed [42]. Researchers studied the process kinetics by using mathematical equation that inclusive of resistance by external and internal mass transfer, fluid velocity along the column and type of flow along the column. Large scale effluents need continuous flow as the volume is high and continuous flow provide advantage for cyclic adsorption/desorption. The breakthrough curves obtained from mathematical calculation determined the life span of a column bed and its regeneration time [43]. Only few literatures reported on metal removal via continuous mode [36,44-47]. Based on kinetic models established by previous researcher, kinetic of fixed-bed (or packed bed) model can be determined through the breakthrough curve. As presence of heavy metals from industrial effluent possesses high environmental risk, industries employed fixed-bed column for their adsorption process. The industry scale adsorption runs in the continuous mode due to high volume of wastewater. Industry looking for the column adsorption method by knowing the advantages of the model are simple and reliable. Few dynamic bio-adsorption studies have been reported since past decade [48]. Also, some adsorbents studied for copper ions removal via fixed-bed adsorbent such as coconut-shell [49], chitosan immobilized bentonite [50], zeolite/cellulose acetate blend fibre [51] and rice husk-based activated carbon [52] were published. Another researcher attempted to eliminate Nickel ions using activated carbon extracted from sugarcane bagasse [53] and tea factory waste [54]. In summary, adsorption is more beneficial compared to other water treatment techniques available as it is easy to operate, lower cost of operation and simplicity of design [55].

2. Experimental Procedure for Batch Study

Batch experiments for adsorption is common for laboratory scale study. It was done to evaluate the adsorption isotherms of metal ions onto surface of adsorbent. Figure 1 show the general batch adsorption process. In literature reported by Desta [56], waste water obtained from MAA garment was used for the adsorption study. Adsorbent and adsorbate solution were mixed in a 250mL glass flask and were shake at a constant speed and sufficient contact time for the process to attained equilibrium. The experiment was conducted in room temperature in order to simulate the

environment condition. Next, the experiment was repeated for several times to get more accurate result and mean values were used for calculation.

Pandey *et al.*, [57] performed batch tests to study optimum pH, contact time and equilibrium isotherms of Zeolite NaX adsorbent using 250mL conical flask. Firstly, the conical flask was filled with copper ions solution with concentration of 25ppm and the adsorbent was added into the flask. They left the conical flask to shake for 24 hours using shaking incubator in order to reach equilibrium. The pH ranges studied in their literature was from pH 3 to pH 8 while adsorbent dosage varies from 0.5g to 2g. Small number of samples at several intervals were taken for further analysis. In selenium ions removal by RHA done by Gulipalli *et al.*, [58] utilized a controlled shaker having water-bath temperature for their adsorption study. In their experimentation, temperature was varied from 293 K to 323 K and mixture of adsorbate and adsorbent were shaken at constant rate (150 rpm). Effect of several experimental conditions such as adsorbent dosage, pH, contact time, initial concentration of metal ions was demonstrated in their literature [58].

Tsai *et al.*, [59] attempted to remove lead ions from liquid solution using series of zeolites group adsorbent and activated carbon. Lead ions with concentration of 50 mg/L was mixed with 0.1 g of adsorbent in 125 mL bottles and shaken at 125rpm. The temperature of experiment was constant at 23°C. Analysis were made using Orion model 9682 ion with series lead electrode at selected period of contact time which was 3, 24, 48 and 144 hours.

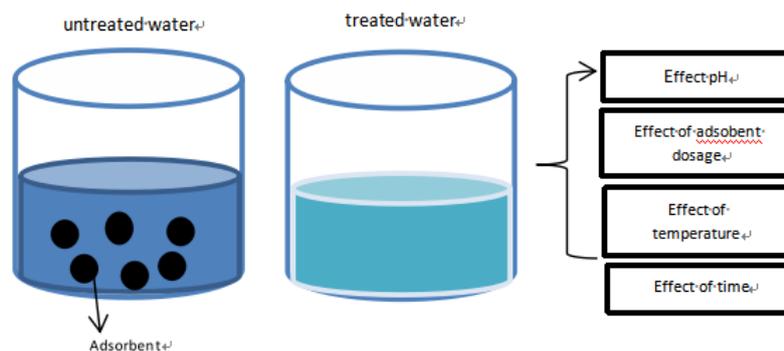


Fig. 1. Batch adsorption process

2.1 Batch Adsorption Study: The Effect of Contact Time

One of crucial parameters that influence adsorption performance is a contact time. Contact time demonstrated the removal percentage of metal ions from solution with respect to the time. Initially, the rate of adsorption will increase significantly and gradually reaching equilibrium at contact time around 60 minutes. It varies depending on type of adsorbent and pollutant itself. After reaching its optimal point of contact time, equilibrium concentration does not have a significant change [56]. Researchers attempted to study batch adsorption of different Copper ions concentration at the same contact time [57]. Results revealed that percentage removal increases with time and became saturated at contact time between 60 minutes to 120 minutes. As a for mentioned, the rate of removal is significant at initial of adsorption but became slower when reaching the equilibrium. Increasing the contact time, no further adsorption was observed as remaining metal ions became asymptotic with time axis.

Gulipalli *et al.*, [58] investigated influence of contact time on Selenium ions adsorption onto surface of rice husk ash coated with ferric chloride solution (RHA). It was discovered that removal rate of Se(IV) ions was very fast. This was due to many active sites available on the adsorbent surface for the ions to bind at starting of the process. However, the vacant sites became harder to be

occupied because the presence of forces between solute on solid phase and bulk in liquid phase that is repulsive to each other. Then, the final ions concentration remained almost similar to each other after contact time from 120 min to 180 min with difference of less than 1% observed after 300 min of contact time. Therefore, they assumed that the process was at steady-state and quasi-equilibrium situation distinguished at 120 min. It was also noted that pH was kept constant during the experiments. In addition, when the adsorbent area is achieved with dynamic equilibrium, there will no more increases in adsorption will occur [60,61].

2.2 Batch Adsorption Study: The Effect of pH

Along with contact time, effect of pH is also critical in adsorption process. From a reported study, they highlighted that percentage of metal ions adsorption was affected by the solution pH. Desta [56] carried out adsorption using Activated Teff Straw (ATS) as adsorbent to remove metal ions by varying its pH from pH 1 to pH 11. The optimal pH for adsorption was noted at pH 6.5 where the removal percentage was the highest. Beyond pH 6.5, the percentage of adsorption experience a sudden drop due to decreasing electrostatic force between adsorbent and adsorbate [8,56]. Other study on effect of pH on removal of Copper ions by Zeolite NaX was demonstrated by Pandey *et al.*, [57]. They conducted the experiment at pH range of 3 to 8 and the result was significant. At pH 6, Copper ions was removed efficiently by the adsorbent but at acidic condition of less than pH 4.5, the removal efficiency was found to be low. Meena *et al.*, [8] stated that pH below than 4.5 is not suitable for zeolites. Also, lower efficiency of adsorption at low pH is due to collapse of zeolites structure [62,63].

Initial pH of Selenium ions with concentration, $C_0=100\mu\text{g/L}$ was pH 6.46 [58]. However, after adding RHA, the pH changes. They conducted study of Selenium removal at pH 2 to 10 and recorded the percent of removal at equilibrium. Ion molecules found in the solution are selenite, biselenite and selenious acid. It was reported that maximum adsorption is at acidic environments, pH 2 to 3. This is due to predominant ion having positive charge which is selenious acid that contain H^+ . Biselenite ion with negative charges are dominant at pH range of 3.5 to 9.0 while further increase in pH makes selenite species to be the predominant ions in the solution. Thus, adsorption performance decline at alkaline condition due to decreasing biselenite ions. Biskup *et al.*, [17] also study the performance of adsorption when pH was varies. They used Zeolite NaX to eliminate heavy metals from solution. They suggested that adsorption process is a combination between two mechanisms; ion exchange and precipitation. Studies on zeolites group such as chabazite, clinoptilolite and activated carbon discovered that different pH has significant changes in adsorption performance. Chabazite was recorded to adsorb metal ions effectively at pH 4 to 11 while clinoptilolite at pH 3 to 11. For activated carbon, the maximum adsorption was noted at pH above neutral. It is expected that zeolites would be a good adsorbent for removal of lead ions at Barksdale Air Force Base where the soil pH was found to be in range 6 to 8 [63].

2.3 Batch Adsorption Study: The Effect of Temperature

Desta [56] carried out investigation on effect of temperature to the adsorption performance of ATS. It was done in five different temperatures; 298, 308, 318, 328 and 343 K. They concluded that increase in temperature also lead to increment in adsorption efficiency. Similar conclusion was reported by Pandey *et al.*, [57] where they conducted study on removal of Copper ions (25ppm) at different temperature. Higher temperature resulted in higher adsorption. Next, Gulipalli *et al.*, [58] performed laboratory scale adsorption by varying temperature from 293 K to 323 K using RHA. Equilibrium metal uptake of the metal ions tested was found to be increasing when the temperature

increase. This phenomenon was discussed to happen due to swelling of adsorbent when there is rise in temperature which allows more sites for binding with metal ions. 323 K was discovered to be the optimal temperature for maximum adsorption of selenium ions by RHA adsorbent.

The same for zeolites adsorbent, efficiency of metal removal increase as the temperature increase. At slightly higher temperature, Chabazite adsorbent resulted in significant improvement of pollutant removal while clinoptilolite produced linear increment with the increasing temperature. However, activated carbon was different in which the temperature change does not affect the adsorption efficiency. It is also proposed that temperature range of 23 to 45 °C is the most suitable for adsorption process by zeolites adsorbent [59].

2.4 Batch Adsorption Study: The Effect of Adsorbent Dose

Removal percentage of metal ions increased when adsorbent dosage increases. Desta [56] increased the amount of adsorbent ATS in adsorption of five different types of heavy metals. Results from the experiment revealed that Nickel ions adsorption was 88%, Cadmium ions 82.9%, Copper ions 81.5%, Chromium ions 74.5% and Lead is the lowest compared to other heavy metals with removal percentage of 68.9%. Study on RHA adsorbent to remove selenium ion showed an optimum potential when adsorbent dosage is 6g per litre of ions solution [58]. However, performance enhancement is only for several addition in adsorbent dosage, and after certain value the performance will gradually become constant and does not have notable increment. Increase in adsorbent dosage indicates more surface area available for adsorption and greater adsorption sites. When adsorbent dosage is below the optimum value, the removal of metal ions is low due to lower binding sites available for adsorption.

2.5 Batch Adsorption Study: The Effect of Initial Ion Concentration

In the view of batch adsorption, the efficiency of adsorption will be affected by initial ion concentration. Rajvinder Kaur *et al.*, [64] stated that the increases of initial ion concentration effect the decreases of the removal metal ion. It is supported by Aksu and Donmez [65], adsorbent will become saturated at a certain concentration because of the availability of adsorbent active site. The equilibrium adsorption capacity, q_e will rise with increasing of initial ion concentration even though the percentage of metal ion elimination decreases. The increment of adsorption rate will be influence by initial concentration of adsorbate particle [66]. The rate of collision between the particle in adsorbate will be low with lower initial ion concentration. It causes the precise increment of adsorption capacity. In addition, the accomplishment of equilibrium between adsorbate initial ion concentration and adsorbate metal ion make no more increment in adsorption rate capacity [67].

2.6 Batch Adsorption Isotherms: Equilibrium Model

In adsorption systems, the amount of solute adsorbed increases until reaching the equilibrium. Equilibrium is the state of the system at which the rates of adsorption and desorption are equal. In other words, equilibrium is a dynamic state at which both adsorption and desorption are occurring simultaneously at the same rate so that no further net adsorption takes place [68]. The equilibrium state is characterized by a certain solute concentration on the adsorbent (x , mg of adsorbate/gram of adsorbent) and an associated final solute concentration (C_e) in the liquid phase. These parametric values can be fitted to one or more standard isotherm equations so that they can be expressed in a mathematical form. This procedure will help in designing batch and column [62]. Theoretical and

empirical equation to calculate experimental isotherms has been introduced previously [69,70]. Most of theories available are on solid-gas systems as it is less complicated compared to aqueous. However, statistical theories for solid-gas are also applicable for liquid-solid systems and common isotherms used in adsorption calculation are Freundlich and Langmuir isotherm [68]. Isotherms equation are utilized for optimization of adsorbent, taken into account the concentration of adsorbate. For design optimization, appropriate correlation should be applied to get a proper process equilibrium curve [71]. Calculation of adsorption isotherm is the most common way to study the mechanism of adsorption process [72].

2.6.1 Langmuir isotherm

Theoretical equation proposed by Langmuir's can be applied to adsorption on a perfectly smooth surface with no interaction between the adsorbed molecules. This isotherm is similar to ideal gas equation and adsorption that obeyed Langmuir's isotherm are called ideal adsorption [69]. Presence of mono layer adsorbate at surface of adsorbent are predicted by Langmuir model [73]. Assumptions made is the molecules of pollutants does not interact with each other and the enthalpy is independent of surface. Therefore, finite number of sites are available for adsorption to occur [74]. Another assumption is energy of bond created between the surface and adsorbent are equal for all sites. As there are fixed sites number per unit adsorbent, adsorption will take place when all sites are occupied.

Linear equation for Langmuir isotherm:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{bq_0C_e} \quad (1)$$

Where C_e is concentration of metal ions or adsorbate (mg/L), q_e the equilibrium capacity of adsorbate on the adsorbent (mg/g), q_0 is mono layer adsorption capacity (mg/g) and b defines Langmuir constant (L/mg) which related to adsorption free energy.

2.6.2 Freundlich isotherm

Deviations from the Langmuir equations are often observed. This may be because the surface is not uniform, and also may be due to interactions between the adsorbed molecules. Pollutants attached to the surface of adsorbent make it complicated for other molecules to attach to neighbouring sites. This led to deviation from ideal adsorption and Langmuir isotherm is not suitable to be employed. Another reason for deviation from Langmuir isotherm is that there is a possibility of multi-layer adsorption. The adsorption isotherm discloses the relationship between adsorbate concentration and its degree of accumulation onto the adsorbent surface at a constant temperature. Since data obtained from batch adsorption is not applicable to represent equilibrium adsorption by packed bed column, data from modeled packed bed operation can fit this isotherm model [17].

Linear form of Freundlich isotherm:

$$\log q_e = \log k_f + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

where k_f defines Freundlich constant while n is dimensionless constant, indicating the adsorption capacity and intensity. Table 1 show the summary of frequent isotherm model equation used for the batch adsorption.

Table 1
Summary of isotherm model equation for batch adsorption

Isotherm Model	Equation non-linear form	Equation linear form	Parameter	Ref.	
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	Type	Equation	q_e (mg/g): equilibrium adsorption capacity Q_{max} (mg/g): maximum adsorption capacity K_L (L/mg): Langmuir constant	[75]
		I	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	C_e (mg/L): equilibrium adsorbate concentration	
		II	$\frac{1}{q_e} = \left[\frac{1}{q_m K_L} \right] \frac{1}{C_e} + \frac{1}{q_m}$	C_0 (mg/L): initial concentration R_L Separation factor	
		III	$q_e = q_m - \left[\frac{1}{K_L} \right] \frac{q_e}{C_e}$		
		IV	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$		
Freundlich	$q_e = K_f C_e^{1/n}$	$\log q_e = \log K_f + \left(\frac{1}{n} \right) \log C_e$	K_f (mg/g)(L/g) ^{1/n} : Freundlich constant n : Heterogeneity factor	[76]	

2.6.3 Adsorption kinetic model: Pseudo first order, Pseudo second order and Intra particle diffusion (ID)

To specify the rate of adsorption of various heavy metal onto the adsorbent, pseudo first order, pseudo second order and intra particle diffusion model were used as a kinetic model. All the linear form and nonlinear form of model are summarized at Table 2. Whereas the Table 3 shows the comparison of maximum adsorption capacity, q_e (mg/g) for other various adsorbate used.

Table 2
Summary of kinetic model for batch adsorption

Kinetic model	Non-linear equation	Linear equation	Parameter	Ref.	
Pseudo first order	$q_t = q_e(1 - \exp^{-k_1 t})$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$	q_t (mg/g): Amount of adsorbate at time k_1 (min ⁻¹): Pseudo first order rate constant	[77]	
Pseudo second order	$q_t = k_2 q_t^2 t$	I	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) \frac{1}{q_e} + \frac{1}{q_e}$	k_2 (g/mg/min): Pseudo Second Order rate constant	[78]
		II	$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) \frac{1}{t} + \frac{1}{q_e}$		
		III	$\frac{1}{t} = \frac{k_2 q_e^2}{q_t} - \frac{k_2 q_e^2}{q_e}$		
		IV	$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t$		
Intra particle diffusion (ID)		$q_t = K_i t^{0.5}$	k_i (mg/gmin): intraparticle diffusion rate constant	[79]	

Table 3
 Comparison of maximum adsorption capacity, q_e (mg/g) for other various adsorbate

Adsorbate	Adsorbent	Parameter	Isotherm and kinetic model	q_e (mg/g)	Ref.
Pd^{2+}	GA 2-aminopyridine glyoxal Schiff's base		Langmuir and pseudo-second-order	166.7	[80]
Pb^{2+} and Cu^{2+}	γ - Fe_2O_3 nanoparticles		Freundlich, Langmuir, pseudo-second-order model	$Pb^{2+}=68.9$ $Cu^{2+}=34.0$	[81]
Cd^{2+}	Phosphate modified activated bamboo	pH, contact time, adsorbent	Langmuir and pseudo-second-order	202.55	[82]
Methylene blue (MB)	Fly ash- based geopolymer	dosage, Initial concentration	Langmuir and pseudo-second-order	37.04	[83]
Methylene blue (MB)	Biomass FA-geopolymer		Langmuir and pseudo-second-order	15.4	[84]
Pb^{2+}	Poly (itaconic acid)		Langmuir and pseudo-second-order	734.3	[85]
Hg^{2+}	Poly (maleic acid)		Langmuir and pseudo-second-order	870.1	[86]
Hg^{2+}	Triethylene-tetramine grafted		Langmuir and pseudo-second-order	1044	[87]
Cd^{2+}	Molybdenum disulphide	pH and contact time	Langmuir and pseudo-second-order	477	[88]
Cd^{2+}	Nano composite	pH, contact time, adsorbent dosage, Initial concentration	Langmuir	148.32	[89]
Hg^{2+}	d- MoS_2/Fe_3O_4 nanohybrids	Contact time	Langmuir and pseudo-second-order	425.5	[90]
Pb^{2+}	benzene-1,3,5-triamine, paraformaldehyde	pH, contact time, adsorbent dosage, Initial concentration	Freundlich and Intraparticle diffusion	3.05	[91]
Hg^{2+}	Carbon nanotube + magnetite cobalt sulfide nanohybrid	pH, contact time, adsorbent dosage, Initial concentration	Langmuir and pseudo second order	1666	[92]

Adsorbate	Adsorbent	Parameter	Isotherm and kinetic model	q_e (mg/g)	Ref.
Pb ²⁺ Cu ²⁺ Ni ²⁺	Soy waste biomass	pH, contact time, adsorbent dosage, Initial concentration	Freundish and pseudo second order	0.4089mmol/g 0.6841mmol/g 0.6705mmol/g	[93]
Cu ²⁺ Co ²⁺ Ni ²⁺ Pb ²⁺ Cd ²⁺	Dextran-Chitosan	pH, contact time, adsorbent dosage, Initial concentration	Langmuir and Pseudo second order	342 232 184 395 269	[94]
Ni ²⁺	MLTA-P + Faujisite (FAU) zeolite	pH, contact time, adsorbent dosage, Initial concentration	Langmuir and Pseudo second order	100	[95]
Co ²⁺	-Powder nanolimestone - limestone	pH	Langmuir and pseudo first order	60 17.1	[96]
Selenium (IV)	-Zeolite synthesis from Low calcium fly ash -Zeolite synthesis from high calcium fly ash	pH, contact time, adsorbent dosage, Initial concentration	Freundish and pseudo second order	4.16 3.93	[97]
Pb ²⁺	- Bean husk - fish scale	pH, contact time, adsorbent dosage Initial concentration, temperature	Langmuir and pseudo second order	-12.66 - 11.51	[98]
Cd ²⁺	-henna -henna + Chitosan	pH, contact time, adsorbent dosage, Initial concentration	Langmuir, Freundish and Pseudo second order	-16.835 -23.866	[99]
Cd ²⁺	Nickel Oxide/CNT Nanocomposite -s	pH, contact time, adsorbent dosage, Initial concentration	Langmuir, Temkin and Pseudo second order	2.54	[100]
Cd ²⁺	Cobalt Oxide	pH, contact time, adsorbent dosage, Initial concentration, temperature	Langmuir, and Pseudo second order	3.679	[101]

Adsorbate	Adsorbent	Parameter	Isotherm and kinetic model	q_e (mg/g)	Ref.
Cd^{2+}	Cajanus cajan Husk	pH, contact time, adsorbent dosage, Initial concentration	Pseudo second order	42.16	[102]
Pb^{2+} Cd^{2+}	Carbon black + sodium bentonite	pH, contact time, adsorbent dosage, Initial concentration	Langmuir, and Pseudo second order	7.69 0.8	[103]
Cr^{3+} Cr^{4+}	Activated carbon from olive waste	pH, contact time, adsorbent dosage, Initial concentration	Langmuir, and Pseudo second order	14.3 74.9	[104]
Mn^{2+}	Saccharum bengalense (Biomaterial)	pH, contact time, adsorbent dosage, temperature	Langmuir and Harkin Jura, pseudo second order	21.72	[105]
Rhodamine B	Fe_3O_4 @polydo pamine core-shell nanocomposite (Fe_3O_4 /PDA)	pH, contact time, adsorbent dosage, temperature	Langmuir, and Pseudo second order	195.3	[106]
Ni^{2+}	Sewage sludge	pH, contact time, adsorbent dosage, Temperature, initial ion concentration	Freundlich, and Pseudo second order	11.53	[107]

3. Experimental Procedure for Column Study

Column study can be done in many ways but usually, researchers applied similar methodology for their work. Figure 2 show the basic design for column adsorption experiment. Nwabanne and Igbokwe [108] performed their packed bed column experiments by using 300 mm length of glass column having internal diameter of 30 mm. Their adsorbents which was activated carbon (diameter range 0.425 mm to 0.6 mm) were packed inside the column. Before, the column was layered with glass wool upon the loading of adsorbent. Bed height was varied to 50 mm, 100 mm and 150 mm. Similarly, Meghna *et al.*, [109] packed the column with glass wool but instead of a layer, they prepared two layer of glass wool at the bottom of column and adsorbent was filled in between the layer. Other researchers prepared adsorbent NCS/SA/MC bead in ratio 2:8:1 in a glass column of 30 cm length [110]. Next, ion solution was fed through the column filled with adsorbent and continuously flow until final concentration approached initial concentration. They studied three different parameters which were influence of bed height, flow rate and initial ion concentration to column adsorption performance. Lin *et al.*, [111] evaluated isothermal performance of their packed

bed column for removal of butanol using KA-I resins. They utilized a glass column of 200 mm Length and 30 mm diameter which can accommodate up to 100 g of resins adsorbent. Water jacket was installed to their adsorber column so that the temperature can be kept constant. At several time intervals, effluent samples were collected for further analysis using gas chromatography.

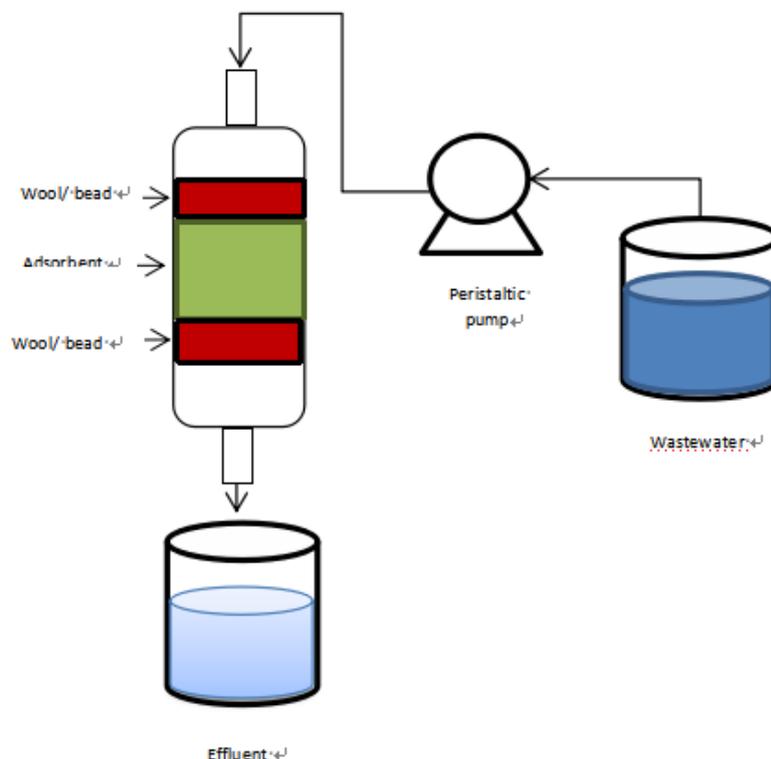


Fig. 2. Basic design of column adsorption

3.1 Column Adsorption Study: Influence of Flow Rate on Breakthrough Curves

Breakthrough point could be affected by several parameters such as flow rate, bed height and initial ion concentration. Based on Sivakumar and Palanisamy [112], breakthrough graph produced a steep curve when flow rate increases and thus, obtained faster breakthrough. Initially, elimination of metal ions was very fast and started to decrease upon reaching saturation. When flow rate increases, residence time for the adsorbate in column also increase, sufficient enough for adsorption process to reach equilibrium. Breakthrough curve for copper adsorption onto NCS/SA/MC bead via column adsorbent was studied by altering the flow rate to 1 mL/min and 1.5 mL/min [110]. Bed height and initial concentration of copper ions was 1.5 cm and 200 mg/L, respectively. From their result, lower flow rate generates longer saturation time and breakthrough time with excellent removal performance than higher flow rate. At higher flow rate, metal ions do not have enough time to bind onto the surface of beads adsorbent. This caused the adsorption performance to decrease.

Next, Lin *et al.*, [111] demonstrated the effect of feed flow rate to the shape of breakthrough curve. They investigated the adsorption of butanol in a packed bed of KA-I resin where resultant curve showed an "S" shape. When flow rate was increased, the curve shifted to the left. They suggested that removal of butanol need longer time when flow rate increase. Shorter time led to low distribution of solution in the column and lower diffusion between adsorbate and adsorbent. Also, at higher flow rate, value of EBRT was reduced. According to Meghna *et al.*, [109], decrease in residence time causing lower efficiency of adsorption when flow rate is high.

3.2 Column Adsorption study: Impact of Bed Height on Breakthrough Curves

Shape of breakthrough curves could also affect by the bed height. From experimental study by Nwabanne and Igboke [108], increasing the bed height resulted in higher removal of ions due to increasing availability of sites for adsorption. In small bed height, ratio of ions concentration is higher than the bed height and the adsorption capacity will be limited as less amount of adsorbent available in small bed height. Vijayalakshmi *et al.*, [110] discussed breakthrough curve from their packed bed column research studies for two bed heights, 1 cm and 1.5 cm. Other parameters such as flow rate and ions concentration were kept constant during the experiment which was 1.5 mL/min and 200 mg/L respectively. Increment in adsorbent bed height causes the saturation time increase and thus, improve the efficiency of removal. Therefore, they concluded that 1.5 cm is the optimum bed height for their research. In reported study by Meghna *et al.*, [109], they increase the bed height of their column adsorbent by adding more Fe₃O₄-SD particles into the column for height of 2 cm, 4 cm and 8 cm. Final concentration of each bed height were 29.42, 18.85, 10.94 mg/g for copper ions and 20.31, 18.08, 9.97 mg/g for nickel ions.

3.3 Column Adsorption Study: Influence of Initial Ion Concentration on Breakthrough Curves

The breakthrough curve was steeper when ion concentration increases during the column tests. This is due to decreasing flux of mass transfer from bulk solution to adsorbent surface as driving force became weaker [112,113]. At higher concentration, there are a large presence of metal ions, so the efficiency of adsorption decreases. However, breakthrough time for higher concentration was said to be shorter than in lower concentration [108]. Also, at higher concentration, there will be many metal ions left after adsorption reach equilibrium and thus, percentage of ion elimination from aqueous solution decrease [110]. Effect of various range of initial metal ion concentration was demonstrated by Babu and Gupta [39]. Similar to [113], column test by Lin *et al.*, [111] also produced steep graph of breakthrough curve when metal ions concentration increase. Higher initial flux was exerted when initial feed concentration increase, resulting the solute to squeeze deeper into matrix. Meghna and co-workers [109] varied the concentration of nickel and copper ions to 10-30 mg/L and analyzed the breakthrough curves at 2 cm bed height. At high concentration, adsorbent got saturated quickly due to higher molecules of adsorbate presence. They concluded that the column can give excellent adsorption performance when feed concentrations is lowered.

3.4 Column Adsorption: Breakthrough Curve

Fixed bed column comprised of adsorbent bed with continuous flow of waste water containing target substance to be eliminated [15]. To design a fixed-bed column for adsorption, breakthrough curves obtained from series of column experimental data are required [65,66]. Figure 3 show the pattern of breakthrough curve. Breakthrough time and curve of the breakthrough graph indicates the dynamic response of the adsorbent system. Therefore, it is critical to calculate varieties of experimental condition related to column studies. Several mathematical analyses were shown in previous literature [43,44,116,117].

Calculation for volume of waste water are as follows:

$$V_{\text{waste}} = Q t_{\text{total}} \quad (3)$$

where V_{waste} is volume of waste water (mL), Q represents volumetric flow rate (mL/min) and t_{total} is the total time of waste water flow (min). To calculate maximum capacity of a column bed, q_{total} (mg/g), equation below should be applied, if area under breakthrough curve (A_c) is known.

$$q_{\text{total}} = \frac{QA_c}{1000} \quad (4)$$

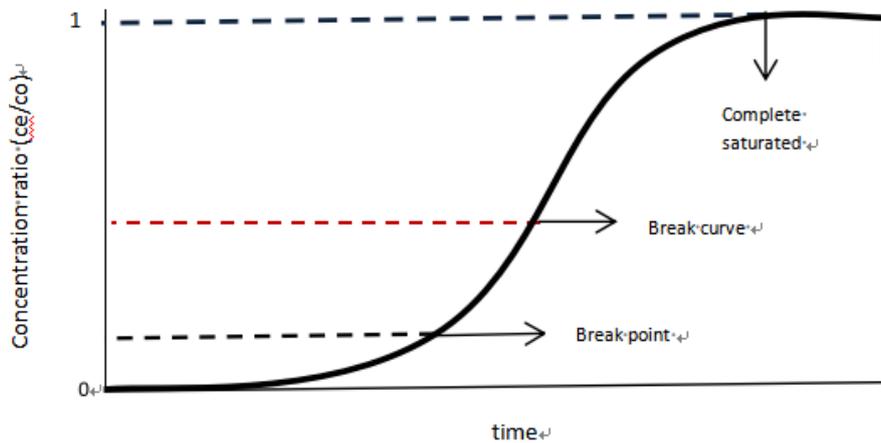


Fig. 3. Breakthrough curve

3.4.1 The Thomas model

According to Kavak and Öztürk [65], Thomas model is known as the bed-depth service-time (BDST) model. This approach was said to be the simplified version of Bohart and Adams's irreversible isotherm model. Thomas model neglected mass transfer resistance from both intraparticle and fluid-film. Thus, this model assumed that surface reaction between ion molecules and unoccupied sites controlled the adsorption rate. Linearized expression for Thomas model is [113,114,118]:

$$\ln \left(\frac{C_o}{C_e} - 1 \right) = \frac{K_t q_0 M}{Q} - \frac{K_t C_o V}{Q} \quad (5)$$

C_o and C_e are the inlet concentration and outlet concentration of solution (mg/L) respectively. M is the total mass of adsorbent (g) while K_t is kinetic coefficient or Thomas rate constant (mL/min/mg).

This model has been applied by various researchers to study kinetics of fixed bed column [112-114]. To obtain value for K_t and q_0 , graph of $\ln [(C_o/C_e)-1]$ versus volume was plotted. High value of regression coefficient, R^2 obtained shows that the model is fitted well with the data from experiments.

3.4.2 The Yoon and Nelson model

Yoon and Nelson model was also widely employed by several researchers in their past work [111,114]. Similar to Thomas model, this model was used to study the kinetics of column adsorption. Gu and Evans [15] stated that estimation by breakthrough curves is critical to obtain successful design of adsorbent column. Experimental data need to be fitted to established models for further optimization of adsorption by packed bed column. The impression from this model is the rate of adsorption decrease by the pollutant particle are equal to adsorption of adsorbent and breakthrough adsorbate to adsorbent [111].

Yoon-Nelson equation [111]:

$$\ln \left[\frac{C_0}{C_e - C_0} \right] = k_{YN}t - \tau k_{YN} \tag{6}$$

where k_{YN} represents Yoon Nelson rate constant (min^{-1}) and τ is time for 50% of adsorbate breakthrough (min). It should be noted that Yoon-Nelson expression is mathematically equal to Thomas model [111]. Table 4 show the summary of various column adsorption model whereas Table 5 show the summary of maximum adsorption capacity for various adsorbent used by column adsorption experiment.

Table 4
 Summary of column adsorption model

Column adsorption model	Linear equation	Parameter	References
Thomas model	$\ln \left[\frac{(C_0)}{C_t} - 1 \right] = \frac{k_{TH}q_0m}{Q} - \frac{k_{TH}C_0V_{eff}}{Q}$	k_{TH} = Thomas rate constant q_0 = maximum solid-phase concentration of the solute	[119,120]
Adam and Bohart model (ABM)	$\ln \left[\frac{(C_0)}{C_t} - 1 \right] = \frac{K_{AB}N_0z}{u} - K_{AB}C_t t$	K_{AB} = Adam and Bohart model rate constant N_0 = adsorption capacity	[119,120]
Yoon–Nelson model (YNM)	$\ln \frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}$	k_{YN} = rate constant	[119,120]
Clark mode (CM)	$\frac{C_t}{C_0} = \frac{1}{(1 + Ae^{-rt})^{1/(n-1)}}$	A = parameter kinetic equation	[119,120]

Table 5
 Summary of maximum adsorption capacity for various adsorbent used by column adsorption

Adsorbate	Adsorbent	Operation parameter	Isotherm model	Maximum adsorption capacity (mg/g)	References
Cr^{2+}	Pistachio shell	Initial concentration ion, flow rate, bed height column, pH, effluent Concentration ion and temperature	Thomas Model, Yoon-Nelson Model, Adam and Bohart model	27.95	[121]
Cu^{2+}	Amino-functionalized ramie stalk based adsorbent	Initial concentration ion, flow rate and bed height column	Thomas Model, Yoon-Nelson Model, Adam and Bohart model	0.528	[122]
Pb^{2+} Cd^{2+}	Magnetic polymer nano-composite	Initial concentration ion, flow	Thomas Model	$\text{Pb}^{2+} = 36.20$ $\text{Cd}^{2+} = 37.25$	[123]

		rate, bed height column, pH and temperature			
Cu ²⁺ Co ²⁺ Ni ²⁺	Sugarcane Bagasse	Initial concentration ion, flow rate and bed height column	Thomas Model, Adam and Bohart model	Cu ²⁺ = 1.060 Co ²⁺ = 0.80 Ni ²⁺ = 1.029	[124]
F ⁻	Magnesium–incorporated hydroxyapatite pellets	initial concentration ion, flow rate, pH, bed height column, particle Size, particle shape	Thomas Model, Adam and Bohart model	45.5	[125]
Cr(VI)	Co-immobilized activated carbon	Initial concentration ion, flow rate and bed height column	Thomas Model	11.7	[126]
As ⁵⁺	Chitosan	Initial concentration ion, flow rate, bed height column, bed diameter, flow direction	Thomas Model, Yoon-Nelson Model, Adam and Bohart model	51.2	[127]
PO ₄ ³⁻	Zirconium-loaded soya bean residue	pH, initial concentration ion, flow rate, bed height and particle size	Thomas Model, Yoon-Nelson Model, Adam and Bohart model	12.21	[128]
BrO ₃ ⁻	Fe ²⁺ /Al ³⁺ layered double hydroxide	Initial concentration, flow rate and bed height	Thomas Model, Adam and Bohart model	71.01	[129]
Arsenoic acid Co ²⁺ Zn ²⁺	carbon nanotube (CNT) coated polyamidoamine dendrimer (PAMAM)	Initial concentration, flow rate and bed height	Thomas Model, Yoon-Nelson Model, Adam and Bohart model	432 494 470	[130]

Conclusion

In many years, an industry always looking for the low-cost operation, high availability of the material used and environment friendly for the water treatment. But unfortunately, adsorption process still leads to high cost operation and higher solid waste adsorbent [131,132,133]. However, for the huge water treatment process, column adsorption become a choice compared to batch

adsorption. Industry demand for efficient operation of water treatment make a researcher need to come with high quality of result for maximum adsorption capacity for the adsorbent used. From all the literature reviewed, we conclude that, all researcher searching for the maximum adsorption capacity for different adsorbent, adsorbate, to fit with isotherm model and kinetic model. Column adsorption study revealed that it is better, simple and economical for removal of heavy metal compared to batch study. All the important parameter for batch adsorption, i.e, contact time, pH, temperature, adsorbent dosage, initial concentration and column adsorption, i.e, inlet ion concentration, flow rate, bed height also have been discussed clearly.

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