

Adsorptive Chromatography: A Sustainable Strategy for Treatment of Food and Pharmaceutical Industrial Effluents 11

Anand S. Gupta, Piyush Kumar, Soumya Pandit, and Ram Prasad

Abstract

Pollution of water bodies is the major threat to environment sustainability mainly in the industrial area. The quality of portable water bodies such as river, lakes and ponds is being tremendously compromised and deteriorated at very high rate by industrial effluents. Different techniques such as trickling-bed reactor, fluidized bed reactor (FBR), packed bed reactor (PBR), membrane process and bubble column reactor (BCR) are being used for treating effluents from different industries. The effluent is mainly composed of colours, heavy metal traces, chemicals, drugs and process-related toxins depending on the sector of industries operated. The effluents from various food and pharmaceutical industries are mainly treated by carbon as a primary treatment for colour and toxin removal, followed by membrane as a secondary treatment for various intermediates. Finally, deodorization and bacterial load reduction by chemical method are employed.

Although various techniques are being utilized, they lack sustainability and agility for effluent treatment, which can be overcome by adsorption phenomenon of chromatographic process. The thermodynamic mechanism in adsorptive chromatography can be strategically used for decolourization, toxin removal, deodorization and bacterial load reduction in a simple one-step strategic approach. The current chapter focuses on various approaches for effluent treatment of food and

A. S. Gupta $(\boxtimes) \cdot P$. Kumar

S. Pandit

R. Prasad

Department of Botany, Mahatma Gandhi Central University, Motihari, Bihar, India

 \oslash Springer Nature Singapore Pte Ltd. 2021

Amity Institute of Biotechnology, Amity University Mumbai, Mumbai, Maharashtra, India

Department of Life Sciences, School of Basic Sciences and Research, Sharda University, Greater Noida, Uttar Pradesh, India

R. Prasad (ed.), *Environmental Pollution and Remediation*, Environmental and Microbial Biotechnology, [https://doi.org/10.1007/978-981-15-5499-5_11](https://doi.org/10.1007/978-981-15-5499-5_11#DOI)

pharmaceutical industry to maintain and sustain the environment and minimize the pollution.

Keywords

Chromatography · Membrane process · Trickling bed · Fluidized bed reactor · Packed bed reactor · Bubble column reactor

11.1 Introduction

Water bodies are being contaminated with different industrial solid waste, discharge and effluents which leads to a detrimental effect on the environment. Amongst the different industries, food and pharmaceuticals are the major contributors to environment hazards. In the food industries, the usage of various colours and additives in formulations such as confectioneries, health supplement and beverages is the key contributor (Singer et al. [2003](#page-19-0)). The pharmaceutical industry produces various active pharmaceutical ingredients (APIs) for formulations. Also, along with API, they too use varied diluents and excipient which may be colouring agents in various degrees of magnitude. Several API are used as drugs for pharmacological effect which includes antibiotics that are used therapeutically for treating infections caused by pathogenic bacteria in human, animal and birds (Cabello [2006\)](#page-17-0). The discharge such as water effluents and drains from food and pharmaceutical industries contributes as a high degree of water pollutants and threats to portable water sources used for human consumptions. The quality of portable water bodies such as river, lakes and ponds is being tremendously compromised and is deteriorating at a high rate due to industrial effluents (Vignesh et al. [2011\)](#page-19-1).

The major challenges of food industries are the coloured discharge in the portable water bodies which not only makes water unfit for human consumption but also adversely affects the flora and fauna of the water bodies. The phenomenon of toxic effect and accumulation into aquatic animal has predominately ruined the aquatic life system which indirectly has effect on portable water quality. Presently, the dyes and colourants used in food industries are synthetic and semisynthetic derivatives or natural origin compounds (Dotto and Pinto [2011\)](#page-17-1). The dyes are chemically composed of reactive functional groups which affect the planktons present in the water bodies which are crucial for food chain of the aquatic system. Hence, these colourants may have a significant impact on the water quality irrespective of the water bodies. Similar challenge also arises for the pharmaceutical industries for dyes used for tablets, granules, lozenges and oral liquids (Hassaan and El Nemr [2017](#page-17-2)).

In the confectionery process, the colourants and dyes mainly enter in the effluent during surface washing of the lozenges for smoothening effect as a critical step for texture improvisation. The surface washing creates a high-throughput volume of effluent in food industries (Ozgun et al. [2012\)](#page-18-0), whereas other steps such as spillages during colour making and addition, mould washing after process, sudden leaks and inevitable discharges through pipe fitting during the process are also contributors in the effluents. The potency of these food dyes has a high degree of risk for marine wealth indicating development of process for decolourization (Husband [2014\)](#page-18-1). The consequences of these adverse effects may be hazardous on the unique species present in the microbial flora and fauna, as well as planktons in water bodies which are essentials for maintenance of chemical oxygen demand (COD) and biological oxygen demand (BOD) (Kanu and Achi [2011](#page-18-2)).

The discharge of effluents from pharmaceutical industries to water bodies introduces chemical agents such as antibiotics which are mainly responsible for potential toxicity and water contamination. These antibiotics are released into the water bodies during production of effluents from pharmaceutical industries and human discharge and disposal. The continuous exposure to antibiotics leads to development of antibiotic-resistant strains that act as a threat to public health (Kim and Aga [2007](#page-18-3); Koch et al. [2021](#page-18-4)). Different antibiotics have been identified in crucial water resources such as groundwater, surface water and streams (Kolpin et al. [2002\)](#page-18-5). Also, other environment-maintaining components such as sewage treatment plant (STP), sludge, soil and sediments are composed of antibiotic residue (Lindsey et al. [2001\)](#page-18-6). Antibiotics are frequently released in large amounts along with municipal wastewater because of their incomplete metabolism by humans or because of the inappropriate disposal of unused antibiotics (Díaz-Cruz and Barceló [2005](#page-17-3)). Such unregulated activities have not only led to emergence and propagation of antibiotic resistance but also lead to issues in wastewater treatment and disposal (Kim and Carlson [2007](#page-18-7)).

Amplified exposure to these antibiotics results in development of antibioticresistant microorganisms that disturb the community structure by entering into a healthy individual and causing diseases (Tandukar et al. [2013](#page-19-2); Koch et al. [2021\)](#page-18-4). This has led to concerns being raised with respect to the possible effects of antibiotic residues present in the aquatic environment. Antibiotics tend to possess allergenic potential and cause side effects and toxicity. The basic classes of antibiotics majorly include beta-lactams derivatives, sulphonamides, tetracyclines, quinolones, aminoglycosides, macrolides, glycopeptides and oxazolidinones (Van Hoek et al. [2011\)](#page-19-3).

11.1.1 Challenges for Effluent Treatment of Food and Pharmaceuticals Industries

The process for effluent treatment has differential aspect involving factors such as engineering and design prospect, high-throughput volume and selection of unit operation; also, the process economics and sustainability are critical consideration. The selection of different unit operations such as horizontal subsurface flow constructed wetland (HSFCW) (Rousseau et al. [2004\)](#page-18-8), upflow anaerobic sludge blanket reactor (UASB) (Lettinga et al. [1980\)](#page-18-9), membrane bioreactors (MB) (Stephenson et al. [2000](#page-19-4)), trickling filter (TF) (Kornaros and Lyberatos [2006\)](#page-18-10), bubble column reactors (BCRs) (Smith et al. [1996](#page-19-5)), airlift reactors (ALRs) (Chan et al. [2009\)](#page-17-4), packed bed bioreactors (PBRs) (Silva et al. [2002](#page-19-6)) and adsorptive

Fig. 11.1 Generalized adsorptive chromatography design for wastewater treatment from pharmaceutical and food industries

chromatography (AC) (Cooney [1998\)](#page-17-5). The major challenges involved in process engineering are increasing volumetric throughput and quality output back into water bodies after treatment.

The adsorptive chromatography is performed mostly in cylindrical column with inlet and outlet control with between lies bed of adsorbent on perforated resting support at bottom (Fig. 11.1). In the adsorptive process, important concern is fluid dynamics of the chromatographic system and accurate process engineering as synergistic effect for efficacy and speed of adsorption process (Hubbuch et al. [2005\)](#page-17-6). Process engineering deals with improving the transport and adsorption of target molecule such as antibiotics from pharmaceutical effluents and dyes and colours from food industries to the adsorption site. The fluid mechanic under flow condition should have reduced mass transfer resistances and axial dispersion (Chihara et al. [1978](#page-17-7)).

The current chapter focuses on various technique and approaches for effluent treatment to minimize the content of various food dyes and pharmaceutical drugs in discharges. The discussion also targets the strategic application of adsorptive chromatography as a tool for reduction and removal of toxic agent from pharmaceutical and food industry's discharge and effluents. The chapter also discusses the

sustainable technique of process dovetailing, which is sequencing of different unit operations for wastewater treatment.

11.2 Techniques for Effluent Treatment from Food and Pharmaceutical Industries

11.2.1 Horizontal Subsurface Flow Constructed Wetland (HSFCW)

An HSFCW is a substantial rock- and sand-filled bowl that is planted with wetland vegetation. It is utilized for tertiary treatment of effluents such as greywater or black water. Solids are expelled in a primary treatment in a septic tank or Imhoff tank. As effluent streams on a level plane through the bowl, the sift material channels through particles and microorganisms decompose the organics. The profluent of a wellworking developed wetland can be utilized for water system and aquaculture or securely be released to accepting water bodies (Wu et al. [2016\)](#page-19-7). Flat stream construction wetlands are generally reasonable to construct where arrival is moderate and can be kept up by the nearby group as no cutting-edge save parts, electrical vitality or chemicals are required (Hammer [1992](#page-17-8)). The outline and execution require master information of hydrodynamics and design for treatment with continuous monitoring of BOD and COD as biochemical aspect (Tilley [2014](#page-19-8)).

11.2.2 Upflow Anaerobic Sludge Blanket Reactor (UASB)

It is a tank process involving an anaerobic treatment for removal of natural poisons and industrial toxins from effluents (Lettinga and Hulshoff Pol [1991](#page-18-11)). Wastewater enters the UASB from the bottom and flow towards upward direction. A suspended slop cover channels and regards the wastewater as it moves through it interacting with microbial flora present in the muck by anaerobic assimilation and changing it into biogas. The solid matters are held by a filtration impact of the cover. The upflow movement of effluents creates mass transfer operation without mechanical system for gas-liquid mixing. The highest point of the reactor permits gases to escape and keep a surge of the slop cover (Fig. [11.2](#page-5-0)). Just like any other oxygen-consuming treatment, UASB require a post-treatment to evacuate pathogens, yet because of a low expulsion of supplements, the water after treatment and solid at slop are utilized as a secondary stream of agribusiness (Tilley [2014](#page-19-8)).

11.2.3 Membrane Bioreactors (MB)

It is a technique which utilizes low-weight microfiltration (MF) or ultrafiltration (UF) with layer filtration gear and slime formation. The slop and films formed are utilized to partition solid and liquid. The enacted slop is utilized as auxiliary and tertiary filtration (Chang et al. [2002](#page-17-9)). The two general operations of MBR

frameworks are vacuum- (or gravity-driven) and weight-driven processes. Vacuum or gravity frameworks are utilizing hollow fibre or flat sheet layers introduced in either the bioreactors or tank. Weight-driven frameworks are in-pipe cartridge frameworks (Stoquart et al. [2012](#page-19-9)). The effluent should be pretreated priorly to reduce the solid content and sediments for better efficiency of MB.

11.2.4 Trickling Filter (TF)

TF are organic reactor bed which operates by utilization of oxygen from vicinity. There is presettled wastewater that is continuously streamed over the channel. As the water travels through the pores of the channel, organic matters are utilized and decomposed by the biofilm covering the channel material (Tilley [2014](#page-19-8)). The TB is used as a reactor in which a gas-liquid mass transfer occurs concurrently in downward direction through a fixed bed of catalyst particles where reaction occurs to conversion of toxin in effluents. The term 'trickling filter' has been used because the removal of organic matter by aerobic bacterial action from wastewater streams through a bed. There are biological growths that attach themselves either to a matrix or bed of stone or any other support material over which the wastewater is made to trickle in contact with the surrounding air (Satterfield [1975\)](#page-18-12).

11.2.5 Bubble Column Reactors (BCRs)

Sublation of solvents as a non-foaming effluent treatment method incorporates the advantages of bubble fractionation and fluid extraction without mixers, settlers or consequent downstream treatment (Lucas et al. [2009](#page-18-13)). Previous research on lab-scale BCRs revealed better efficiencies for removal of non-volatile and volatile organic compounds than bubble fractionation, air stripping and conventional liquid-liquid extraction (Smith et al. [1996\)](#page-19-5). There are three transport mechanisms available by which pollutants mainly gases are removed. They are transport by air bubbles, water entrainment due to the rising air bubbles and molecular mass transport across the gas-water interface. After the sublation, soluble antibiotics, dye and suspended microbial debris are removed from the aqueous phase by further diversification to other unit operations, and volatile pollutants are removed from the top zone of BCR (Turhan and Turgut [2009](#page-19-10)).

In the unidirectional transport through air bubbles, the rising of air bubbles in the column leads to partition of both volatile and non-volatile compounds on the bubble surface. The extent of partitioning is determined by equilibrium relationships for bulk-phase partitioning and surface adsorption with a mass balance for the total amount of pollutant carried by a bubble of radius a . In Eq. [11.1](#page-6-0), m is the total amount of pollutant, Γ is the surface concentration of the bubble, and C_v is the concentration of pollutant in the air bubble:

$$
m = 4\pi a^2 \Gamma + \frac{4}{3}\pi a^3 C_V \tag{11.1}
$$

At equilibrium, the concentrations are related to the bulk-phase water concentration through linear relationships:

$$
\Gamma = K_A C_w C_v = H_c C_w \tag{11.2}
$$

where K_A is the interfacial partition constant and H_c is Henry's law constant. When Eqs. [11.1](#page-6-0) and [11.2](#page-6-1) are combined, the following effective air concentration results:

$$
C_{A} = \frac{m}{\frac{4}{3}\pi a^{3}} = \left(\frac{3}{a}K_{A} + H_{C}\right)C_{w}
$$
\n(11.3)

The term in parentheses is the effective Henry's law constant, H. It depends inversely upon the air bubble size.

11.2.6 Airlift Reactors (ALRs)

ALRs have proved to be efficient alternative devices against conventional systems such as stirred tanks and bubble column contactors for the remediation of several antibiotic-contaminated water bodies, even more because their applications range from synthesis of chemicals, culture of plant and animal cells, production of microalgae, fuel gas and contaminated soils. These are cylindrical or rectangular vessel with a gas distributor at the inlet, usually without mechanical moving parts (Fig. [11.3\)](#page-7-0) (Huang and McDonald [2009\)](#page-17-10). The only energy input needed is to inject the aeration gas through a simple sparging system (Brenner et al. [1997](#page-17-11)). ALRs are considered as feasible and sustainable alternatives for stirred tank reactors (STRs), particularly for numerous bioprocesses such as plant and animal cell cultures but also for the treatment of contaminated fluid fluxes (Benyahia and Jones [1997\)](#page-17-12).

The volumetric mass transfer coefficient (k_La) is the rate of gas transfer across the gas-liquid interface per unit of driving force (the driving force is the gas

concentration gradient between the liquid and the gas ΔC) and is defined by the following equation (Cozma and Gavrilescu [2010\)](#page-17-13):

$$
OTR = kLa \Delta C \qquad (11.4)
$$

11.2.7 Fluidized Bed Reactors (FBRs)

The FBRs can be used as a high-throughput system for treatment of liquid effluent and discharges from industries. The phenomenon of fluidization leads to suspension of solid particulates in an upward-flowing stream of liquid. The liquid velocity is critically optimized to suspend the particulate matters, without expulsion from the reactor vessel. The solid particles combine to form the loosened bed quickly and also form a suspension at the top with lesser particle at the top. The fluidized material is quite often a solid, and the fluidizing medium is either a fluid or a gas. The qualities and conduct of a fluidized bed are unequivocally subject to both the solid and fluid or gas properties. Before the reactor has begun, the catalyst pellets lie on a mesh at the base of the reactor which later in process converts hazardous pollutants to non-hazardous moiety. Reactants are pumped into the reactor through a distributer consistently making the bed fluidized. The bed's conduct after introductory fluidization relies upon the condition of the reactant. In the event that it is a fluid, the bed grows consistently with expanded upward stream of the reactant (Fig. [11.4\)](#page-9-0).

11.2.8 Packed Bed Bioreactors (PBRs)

The PBRs also known as fixed-bed bioreactors use particulate or immobilized biocatalysts throughout vertical tube which is completely packed beads of biocatalysts. Through this packed bed system, the effluents are introduced in through either the bottom or top of the column, and this creates the continuous liquid occupancy in PBRs. PBRs have a low attrition and impact on biocatalyst as compared to STR. PBRs are commercially used for wastewater treatment by using immobilized enzymes and cells for the production of amino acid and organic acid and also the transformation of antibiotics such as penicillins. The particles must be incompressible, and it also has to endure their own weight in PBRs without deformities or blocking the fluid flow pattern. Between the liquid medium and solid catalyst, mass transfer is carried out at high liquid flow rates through the bed, and in order to attain this, the packed beds are frequently operated with liquid recycle (Warren et al. [1976\)](#page-19-11).

The mass transfer coefficient k_s should be known even before an account for external mass transfer effects can be made. k_s is based on the hydrodynamics of the reactor and properties of liquid state of matter, namely, viscosity, density and diffusivity. Values of k_s can be approximately estimated using correlations from existing literature (Moo-Young and Blanch [1981](#page-18-14)):

Fig. 11.4 Fluidized bed reactor for effluent treatment in food and pharmaceutical industries

$$
Re_p
$$
 = (particle) Reynolds number = $\frac{D_p u_{pL} \rho_L}{\mu_L}$
\n Sc = Schmidt number = $\frac{\mu_L}{\rho_L \mathcal{D}_{AL}}$
\n Sh = Shervood number = $\frac{k_s D_p}{\mathcal{D}_{AL}}$
\nAnd : Gr = Grashof number = $\frac{g D_p^3 \rho_L (\rho_p - \rho_L)}{\mu_L^2}$

where u_{pL} is the linear velocity of the particle relative to the bulk liquid, D_p is the diameter of the particle, ρ_L is the density of the liquid, μ_L is the viscosity of the liquid, D_{AL} is the molecular diffusivity in the liquid of component A, k_s is the liquid to solid mass transfer coefficient, g is the gravitational acceleration and lastly ρ_p is the density of the particle (Charpentier [1981;](#page-17-14) Warren et al. [1976\)](#page-19-11).

The Sherwood number represents the ratio of overall as well as diffusive mass transfer rates through a boundary layer, and it contains the mass transfer coefficient. The Schmidt number, which is made up of physical properties of the system, depicts the ratio of momentum diffusivity and mass diffusivity. Sc is a constant value for Newtonian fluids at a constant temperature, pressure and composition. The Grashof number, which is important when the particles are neutrally buoyant, presents the ratio of gravitational forces to viscous forces. The form of the correlation that is used to evaluate Sh and thus k_s is based on the flow conditions, the configuration of the mass transfer system and several other factors. As per the above correlations, k_s in a packed bed is based on the liquid velocity around the particles (Warren et al. [1976\)](#page-19-11). Within the range $10 < Re < 104$, the Sherwood number in packed beds has been determined as follows:

$$
Sh = 0.95 \, Re_p^{0.5} Sc^{0.33}
$$

11.2.9 Adsorptive Chromatography (AC)

The general principle of adsorption in chromatography is being governed mainly by three important techniques such as frontal analysis, displacement method and elution method. In accordance to their application, these techniques are used in different adsorptive liquid chromatography such as analytical chromatography (HPLC) and/or preparative chromatography for capturing, isolation and purification of macromolecules (Kasai et al. [1986](#page-18-15)). The AC as a sustainable strategy for treatment of food and pharmaceutical industrial effluent involves frontal analysis method in which binding of the desired molecules can be achieved from a particular mixture stream composed of various molecules (Oka et al. [1989](#page-18-16)). The AC involves different types of thermodynamic interaction involving isotherms for particular interaction of the molecules in the effluents (Thomas [1948\)](#page-19-12). The effluent is composed of multimolecular interaction, which presents a multilayered of interaction, the AC as a tool for effluent treatment involves interaction types such as hydrophobicity and ion exchange between adsorbent and molecule in effluent mixture.

The throughput of the AC depends on the binding capacity of the adsorbent for a particular molecule present in the effluent (Pereira et al. [2003\)](#page-18-17). The adsorbent's adsorptive property in both the interaction is mathematically estimated by breakthrough curve (BTC). The BTC provides the information correlation between the volumes of effluent, binding capacity per mL of adsorbent at a particular flow rate. The mechanism of interaction in BTC also governs the throughput of the designed process (Thomas [1948](#page-19-12)).

11.3 Modes of Adsorptive Chromatography for Treatment of Effluents and Discharge

In AC, the modes of interaction involved are thermodynamic-driven or kineticdriven process. The kinetic-driven process comprises the migration rate of the molecule with linear velocity (V) of the mobile phase, and least interaction between molecules and adsorbents takes place (Guiochon [2002\)](#page-17-15). In thermodynamic process, involvement of high interaction, i.e. binding of the molecules to the adsorbent, is favoured; also, high capacity adds to process synergism. The thermodynamic process should have irreversible binding phenomenon as an important aspect. Both the approaches, mentioned above, have different application; e.g. kinetic-driven processes are used for purification and polishing of niche pharmaceutical and therapeutic molecules (Fig. [11.5](#page-11-0)). The thermodynamic mode can be applied for capturing and isolating desired molecules in diluted stream (Rathore and Velayudhan [2002](#page-18-18)). The capturing of different class of antibiotics from the effluents of pharmaceutical industries is a good example (Hwang et al. [1994](#page-18-19)). Also, varied class of dyes with different functional group can be captured in AC specifically (Adachi et al. [2002](#page-17-16)).

The modes of AC practised for high-throughput system in treatment of industrial effluents and discharge are thermodynamic-driven process. Thermodynamic-driven AC process can be a positive or negative chromatography. In positive chromatography, the target molecule with high interaction or affinity binds to the adsorbent, whereas negative chromatography involves binding of impurities, and target molecules remain in mobile phase. The most adopted technique for effluent treatment is positive chromatography in which the spectra of target molecules such as antibiotics, colour and dyes, toxins, proteins, peptides, sugar and organic acids are

Fig. 11.5 The thermodynamic- and kinetic-driven process in adsorptive chromatography

Fig. 11.6 Effluent treatment by using positive mode of AC

specifically bound to the adsorbent, and then, the treated water as effluent is introduced in the water bodies (Lee et al. [2014\)](#page-18-20) (Fig. [11.6](#page-12-0)). Selection of AC as positive or negative chromatographic step is influenced by concentration of target, volume of effluent, regeneration of adsorbent after each cycle in process and mechanical stability of adsorbent at such high-throughput level of operation in the process.

Thermodynamic AC mode of operation involves steps such as equilibrium, loading, washing, elution and regeneration as a one complete cycle in the process. These steps are generally utilized for therapeutic molecule purification as AC operation. The thermodynamic mode for effluent treatment can be achieved by implicating frontal analysis technique in which the steps are curtailed to equilibrium, loading (capturing) and regeneration as one complete cycle. The ability to regenerate after each cycle makes AC as a choice of unit operation for process development and also grants techno-economic feasibility (Rathore and Velayudhan [2002\)](#page-18-18).

As frontal technique is the principle underlying AC process which depends on the differential binding affinity, the molecule with high binding affinity will occupy the sites present on chromatographic bed plates from inlet zone till the bed is completely occupied (Ghorai and Pant [2005](#page-17-17)). Once the bed is saturated with molecule, the inlet and outlet concentration from the column will be equivalent. The molecule with highest affinity for the site on adsorbent will elute late, whereas molecule with low affinity will elute earlier in the process (Kasai et al. [1986](#page-18-15)). The target molecules from pharmaceutical and food industry effluents are composed of various antibiotics and colour dyes, respectively (Yoshida and Takemori [1997](#page-19-13)). The binding capacity in AC of a thermodynamic-driven process with positive mode approach is estimated by

BTC (Fig. [11.7\)](#page-13-0). The plot is composed of C/C_i vs cumulative volume (mL) where 'C' is the concentration (mg/mL) of binding molecule at time (t) in minutes from outlet, whereas ${}^{\prime}C_i$ is the initial concentration of binding molecule in effluent load (Aksu and Gönen [2004](#page-17-18)):

$$
BTC = \frac{C_i X V}{V_B}
$$

where V is the breakpoint volume at 10% of BTC and V_B is the bed volume of the column used for BTC.

The degree of binding in thermodynamic approach should have to be irreversible for reusability of the process. The quantification extent of binding depends on the number of site present on adsorbent surface and its area. The interaction on the site present on the chromatographic adsorbent is studied on the basis of the isotherms. These isotherms can be observed as linear or non-linear mechanism of binding depending on the plot of O v/s C^* , where 'O' is the amount of molecule adsorbed per gram of adsorbent (g/g) and C^* is the equilibrium concentration of the molecule in liquid phase (Fig. [11.8](#page-14-0)). The rate of these isotherms depends on their patterns predicted by observing plots as linear and non-linear. These isotherms are used to predict the mechanism of interaction such as types of diffusion in mass transfer of the high-throughput system for industrial effluent treatment (Ghorai and Pant [2005](#page-17-17)).

The mathematical models mostly for isotherm determination of adsorption phenomenon are Langmuir and Freundlich pattern for treatment of effluent from industries which is composed of multiple components and always signifies a non-linear behaviour of adsorption. The following equations are used for studying the non-linear mathematical model and their linearized form for precise estimation of slope and other variables of non-linear models (Kasai et al. [1986](#page-18-15)):

$$
Fremdlich isotherm: \tQ = K_f.C^{1/n} \t(11.5)
$$

Linearized form of Freundlich isotherm : $log Q = log Kf + 1/n log C$ (11.6)

The plot of logQ vs logC provides the straight-line equation to estimate K_f and n which are Freundlich constant indicating the adsorption capacity and adsorption intensity, respectively:

$$
Langmuir isotherm: Q = \frac{Qmax Kl C}{1 + Kl C}
$$
 (11.7)

Linearized form of Langmuir isotherm :
$$
\frac{1}{Q} = \frac{Kl}{Qmax C} + \frac{1}{Qmax}
$$
 (11.8)

The plot of 1/Q vs 1/C will give a straight-line equation, where Q is the quantity of solute adsorbed per unit of adsorbent, C is the concentration of protein in solution, Qmax is the maximum quantity adsorbed at high C and $K₁$ is the dissociation constant which is a measure of strength of binding of solute to adsorbent.

In thermodynamic system for industrial effluent, treatment selection of stationaryphase and effluent-phase environment is critical for process engineering and design. The particle size of the adsorbents also has major consideration as a critical parameter for column designing for such high-throughput system for treatment of industrial effluent. It is technically wise to choose particle size with larger particle size so as to reduce the pressure drop across the operating column at process scale-up from bench level to process scale. The binding capacity is the important factor for selection of adsorbent in any mode of AC process. It is always a target to achieve optimum loading (g of molecule/g of adsorbent) and also to enhance loading on the column by increasing the aspect ratio (D/h) (Rathore and Velayudhan [2002](#page-18-18)).

11.4 Dovetailing of Unit Operations for Sustainable Technique

The emerging trend to treat effluent from industrial sectors and maintain the ecological balance in the water bodies as a mandate from different officials has led to process dovetailing. The dovetailing involves the correct sequencing of various unit operations to get the resultant outcome with recyclable quality for daily reuse or re-entering in water bodies (Bijan and Mohseni [2005\)](#page-17-19). The general theme practised traditionally is alone natural-based operations such as HSFCW, UASB and TF which depends on the bed formation or wet land generation with plantation (Champagne et al. [2017](#page-17-20)). The single-unit operation cannot serve the objective of removal of antibiotics, colours, dyes, drug traces, toxic protein and peptides, fats and carbohydrates (Høibye et al. [2008](#page-17-21)). The dovetailing strategies by combining with correct sequence such as ALRs-AC, AC-TF, FBRs-AC, TF-MB-AC, FBRs-ALRs and AC-AC2 as a tandem approach (Qiu et al. [2013\)](#page-18-21). The dovetailing of AC with other unit operation has not been practised widely, whereas the tandem approach of AC can be used for pharmaceutical and food industry effluent and discharge (Gennaro et al. [1989](#page-17-22)) (Fig. [11.9](#page-15-0)).

The AC1 and AC2 can be selected based on the molecular descriptors such as molecular weight, size and structure, functional group charge, hydrophobicity, conductivity and density for capturing and isolation of the hazardous and toxic molecule in the effluents. The combination of AC1 and AC2 can be followed for ideal sequencing of unit operations (Table [11.1](#page-16-0)).

Fig. 11.9 Treatment of effluents by tandem approach involving AC with different types

AC1	$^+$ AEX	$ {\rm CEX} $	AEX HEC	CEX	\Box HIC	AEX1	CEX1	HIC1
		AC2 CEX AEX HIC AEX HIC CEX AEX2					CEX2	HIC2
AC2	CEX					$AC1$ - AEX - CEX - AEX - HIC - CEX - HIC - $AEX1$ - $CEX1$ - $HIC1$ - $ AEX $ $ HIC $ $ AEX $ $ HIC $ $ CEX $ $ AEX2 $	CEX2	HIC2

Table 11.1 The combination of various AC types in dovetailing process for industrial effluent

11.5 Conclusions and Future Prospects

The conventional methods of effluent management and treatment such as UASB, TF and HSFCW are predominantly dependent on wetland generation and require substantial time lapse and high cost for their construction. Thus, long-term maintenance of such methods is a challenge for sustainability. The adsorption phenomenon in chromatography as strategic approach can be used as an agile and simple and technically feasible method for effluent treatment. The mechanism of AC provides high throughput and sustainability. The model of construction for AC process can be moulded into any stream and outlet with accurate engineering design. The aspect of adsorbent regeneration in AC for higher number of cycle makes it highly economical compared to other techniques. The wide application of AC for specific removal of toxic molecules such as antibiotics, colour and dyes, proteins, peptides, sugar and organic acids from effluent has resulted into a better technique compared to ALRs, PBRs and BCRs. The mass transfer coefficient (kLa) in AC can be easily predicted and understood by isotherm data which provide the engineers an accurate vision for design and process development at various scale.

The concept of dovetailing by hyphenating two different techniques or similar techniques with different types or modes should be explored for effluent treatment from industries of different sectors. The sequencing in the dovetailing process for effluent stream treatment should be correctly performed prior to scale-up models for high-throughput system. The advancements in AC based on types and modes with high binding and site should be utilized for high-volume throughput and scalability, which may provide more efficient and economical process. The correct hyphenation sequence involved in high mass transfer technique such as ALRs, BCRs and FBRs should be utilized amongst or along with AC as strategic approach for rendering water back into mainstream water bodies with enhanced portability. The bacterial and organic load can be easily reduced by MBs and TF as conventional approach for pretreatment of effluents which later can be introduced to AC for enhancing its portability.

The strategic and continuous processes such as tandem approach along with simulation of AC for high-throughput and sustainable technique can be achieved as advancement. Further, utilization of high-end continuous AC technique such as simulated moving bed (SMB) can be used at various scales of process. Liquid-solid continuous fluidized bed (LSCFB), another approach, can also be used for continuous effluent treatment at low rate of method for small-scale industry discharge.

Acknowledgement We thank Dr. Neetin Desai, Director, Amity Institute of Biotechnology, Amity University Mumbai, for infrastructural support. We also acknowledge graduate students Denice Peter and Anuskha Nair for their help in literature survey. The authors also thank Dr. Nilesh Wagh for his editorial help in writing the chapter.

References

- Adachi T, Ando S, Watanabe J (2002) Characterization of synthetic adsorbents with fine particle sizes for preparative-scale chromatographic separation. J Chromatogr A 944:41–59
- Aksu Z, Gönen F (2004) Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. Process Biochem 39:599–613
- Benyahia F, Jones L (1997) Scale effects on hydrodynamic and mass transfer characteristics of external loop airlift reactors. J Chem Technol Biotechnol 69:301–308
- Bijan L, Mohseni M (2005) Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds. Water Res 39:3763–3772
- Brenner A, Ben-Shushan N, Siegel M, Merchuk J (1997) Pilot plant performance and model calibration of a sequencing batch air-lift reactor. Water Sci Technol 35:121–127
- Cabello FC (2006) Heavy use of prophylactic antibiotics in aquaculture: a growing problem for human and animal health and for the environment. Environ Microbiol 8:1137–1144
- Champagne P, Liu L, Howell M (2017) Aerobic treatment in cold-climate countries. In: Current developments in biotechnology and bioengineering. Elsevier, Amsterdam, pp 161–201
- Chan YJ, Chong MF, Law CL, Hassell D (2009) A review on anaerobic–aerobic treatment of industrial and municipal wastewater. Chem Eng J 155:1–18
- Chang I-S, Le Clech P, Jefferson B, Judd S (2002) Membrane fouling in membrane bioreactors for wastewater treatment. J Environ Eng 128:1018–1029
- Charpentier J-C (1981) Mass-transfer rates in gas-liquid absorbers and reactors. In: Advances in chemical engineering, vol 11. Elsevier, pp 1–133
- Chihara K, Suzuki M, Kawazoe K (1978) Adsorption rate on molecular sieving carbon by chromatography. AICHE J 24:237–246
- Cooney DO (1998) Adsorption design for wastewater treatment. CRC press
- Cozma P, Gavrilescu M (2010) Airlift reactors: hydrodynamics, mass transfer and applications in environmental remediation. Environ Eng Manag J 9:681–702
- Díaz-Cruz MS, Barceló D (2005) LC–MS2 trace analysis of antimicrobials in water, sediment and soil. TrAC Trends Anal Chem 24:645–657
- Dotto G, Pinto L (2011) Adsorption of food dyes acid blue 9 and food yellow 3 onto chitosan: stirring rate effect in kinetics and mechanism. J Hazard Mater 187:164–170
- Gennaro R, Skerlavaj B, Romeo D (1989) Purification, composition, and activity of two bactenecins, antibacterial peptides of bovine neutrophils. Infect Immun 57:3142–3146
- Ghorai S, Pant K (2005) Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Sep Purif Technol 42:265–271
- Guiochon G (2002) Preparative liquid chromatography. J Chromatogr A 965:129–161
- Hammer DA (1992) Designing constructed wetlands systems to treat agricultural nonpoint source pollution. Ecol Eng 1:49–82
- Hassaan MA, El Nemr A (2017) Health and environmental impacts of dyes: mini review. Am J Environ Sci Eng 1:64–67
- Høibye L, Clauson-Kaas J, Wenzel H, Larsen HF, Jacobsen BN, Dalgaard O (2008) Sustainability assessment of advanced wastewater treatment technologies. Water Sci Technol 58:963–968
- Huang T-K, McDonald KA (2009) Bioreactor engineering for recombinant protein production in plant cell suspension cultures. Biochem Eng J 45:168–184
- Hubbuch J, Thömmes J, Kula M-R (2005) Biochemical engineering aspects of expanded bed adsorption. In: Technology transfer in biotechnology. Springer, pp 101–123

Husband T (2014) The sweet science of candymaking. ChemMatters 10:5–8

- Hwang BK, Ahn SJ, Moon SS (1994) Production, purification, and antifungal activity of the antibiotic nucleoside, tubercidin, produced by Streptomyces violaceoniger. Can J Bot 72:480–485
- Kanu I, Achi O (2011) Industrial effluents and their impact on water quality of receiving rivers in Nigeria. J Appl Technol Environ Sanit 1:75–86
- Kasai K-I, Oda Y, Nishikata M, Ishii S-I (1986) Frontal affinity chromatography: theory for its application to studies on specific interactions of biomolecules. J Chromatogr B Biomed Sci Appl 376:33–47
- Kim S, Aga DS (2007) Potential ecological and human health impacts of antibiotics and antibioticresistant bacteria from wastewater treatment plants. J Toxicol Environ Health Part B 10:559–573
- Kim S-C, Carlson K (2007) Temporal and spatial trends in the occurrence of human and veterinary antibiotics in aqueous and river sediment matrices. Environ Sci Technol 41:50–57
- Koch N, Islam NF, Sonowal S, Prasad R, Sarma H (2021) Environmental antibiotics and resistance genes as emerging contaminants: methods of detection and bioremediation. Curr Res Microbial Sci. <https://doi.org/10.1016/j.crmicr.2021.100027>
- Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999- 2000: a national reconnaissance. Environ Sci Technol 36:1202–1211
- Kornaros M, Lyberatos G (2006) Biological treatment of wastewaters from a dye manufacturing company using a trickling filter. J Hazard Mater 136:95–102
- Lee MFX, Chan ES, Tey BT (2014) Negative chromatography: progress, applications and future perspectives. Process Biochem 49:1005–1011
- Lettinga G, Hulshoff Pol L (1991) UASB-process design for various types of wastewaters. Water Sci Technol 24:87–107
- Lettinga G, Van Velsen A, Sd H, De Zeeuw W, Klapwijk A (1980) Use of the upflow sludge blanket (USB) reactor concept for biological wastewater treatment, especially for anaerobic treatment. Biotechnol Bioeng 22:699–734
- Lindsey ME, Meyer M, Thurman EM (2001) Analysis of trace levels of sulfonamide and tetracycline antimicrobials in groundwater and surface water using solid-phase extraction and liquid chromatography/mass spectrometry. Anal Chem 73:4640–4646
- Lucas MS, Peres JA, Lan BY, Puma GL (2009) Ozonation kinetics of winery wastewater in a pilotscale bubble column reactor. Water Res 43:1523–1532
- Moo-Young M, Blanch H (1981) Design of biochemical reactors mass transfer criteria for simple and complex systems. In: Reactors and reactions. Springer, pp 1–69
- Oka H, Ikai Y, Kawamura N, Yamada M, Harada K-I, Yamazaki Y, Suzuki M (1989) Improvement of chemical analysis of antibiotics: XV. Isocratic high-performance liquid chromatographic methods for the analysis and preparative separation of the components of bacitracin. J Chromatogr A 462:315–322
- Ozgun H et al (2012) Confectionery industry: a case study on treatability-based effluent characterization and treatment system performance. Water Sci Technol 66:15–20
- Pereira MFR, Soares SF, Órfão JJ, Figueiredo JL (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. Carbon 41:811–821
- Qiu G, Song Y-h, Zeng P, Duan L, Xiao S (2013) Characterization of bacterial communities in hybrid upflow anaerobic sludge blanket (UASB)–membrane bioreactor (MBR) process for berberine antibiotic wastewater treatment. Bioresour Technol 142:52–62
- Rathore A, Velayudhan A (2002) Scale-up and optimization in preparative chromatography: principles and biopharmaceutical applications, vol 88. CRC Press
- Rousseau DP, Vanrolleghem PA, De Pauw N (2004) Model-based design of horizontal subsurface flow constructed treatment wetlands: a review. Water Res 38:1484–1493
- Satterfield CN (1975) Trickle-bed reactors. AICHE J 21:209–228
- Silva AJ, Varesche M, Foresti E, Zaiat M (2002) Sulphate removal from industrial wastewater using a packed-bed anaerobic reactor. Process Biochem 37:927–935
- Singer RS, Finch R, Wegener HC, Bywater R, Walters J, Lipsitch M (2003) Antibiotic resistance the interplay between antibiotic use in animals and human beings. Lancet Infect Dis 3:47–51
- Smith JS, Valsaraj KT, Thibodeaux LJ (1996) Bubble column reactors for wastewater treatment. 1. Theory and modeling of continuous countercurrent solvent sublation. Ind Eng Chem Res 35:1688–1699
- Stephenson T, Brindle K, Judd S, Jefferson B (2000) Membrane bioreactors for wastewater treatment. IWA publishing
- Stoquart C, Servais P, Bérubé PR, Barbeau B (2012) Hybrid membrane processes using activated carbon treatment for drinking water: a review. J Membr Sci 411:1–12
- Tandukar M, Oh S, Tezel U, Konstantinidis KT, Pavlostathis SG (2013) Long-term exposure to benzalkonium chloride disinfectants results in change of microbial community structure and increased antimicrobial resistance. Environ Sci Technol 47:9730–9738
- Thomas HC (1948) Chromatography: a problem in kinetics. Ann N Y Acad Sci 49:161–182
- Tilley E (2014) Compendium of sanitation systems and technologies. Eawag
- Turhan K, Turgut Z (2009) Decolorization of direct dye in textile wastewater by ozonization in a semi-batch bubble column reactor. Desalination 242:256–263
- Van Hoek AH, Mevius D, Guerra B, Mullany P, Roberts AP, Aarts HJ (2011) Acquired antibiotic resistance genes: an overview. Front Microbiol 2:203
- Vignesh R, Karthikeyan B, Periyasamy N, Devanathan K (2011) Antibiotics in aquaculture: an overview. South Asian J Exp Biol 1:114–120
- Warren L, Warren L, McCabe W, Smith JC (1976) Unit operations of chemical engineering. Mc Graw Hill Company
- Wu J, Feng Y, Dai Y, Cui N, Anderson B, Cheng S (2016) Biological mechanisms associated with triazophos (TAP) removal by horizontal subsurface flow constructed wetlands (HSFCW). Sci Total Environ 553:13–19
- Yoshida H, Takemori T (1997) Adsorption of direct dye on cross-linked chitosan fiber: breakthrough curve. Water Sci Technol 35:29–37