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Making GAC adsorption affordable

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Making GAC adsorption affordable

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TWO CRUCIAL USES of granular activated carbon (GAC) in water/wastewater treatment are the removal of synthetic organic chemicals (SOCs) and the removal of natural background organic matter (BOM) that may produce undesirable disinfection by-products (DBPs). However, this treatment process may prove to be expensive if not properly designed. The objective of this paper is to provide an outline of the adsorption theory and the mechanisms responsible for adsorption process, thus identifying the critical factors controlling the adsorption process and to illustrate their role in designing the process to be cost-competitive.

Theoretical framework

During the adsorption process, dissolved organic contaminants from aqueous solution are transported into the porous solid sorbent grains by means of diffusion and are then adsorbed onto the extensive inner surface of the adsorbent. In GAC treatment, water to be treated is passed through fixed or semi-fixed beds which contain GAC. These beds are commonly referred to as adsorbers or filters.

Within a single GAC adsorber, a zone of active mass transfer, in which the adsorbate molecule migrates from bulk solution into the adsorbent, develops after a certain time interval and slowly travels down the bed. The beginning of the breakthrough is achieved, when the front of the zone reaches the end of the bed. The portion of GAC passed by the zone of active mass transfer, can no longer remove the adsorbate and is said to be saturated with adsorbate.

The GAC adsorption process can be described by the following mechanisms:

- a) Mechanisms responsible for transporting the adsorbate through the column (axial transport of adsorbate in the mobile phase).
 - i) Advective flow.
 - ii) Axial dispersion and diffusion (this mechanism is of negligible level in most of the field cases).
- b) Mechanisms responsible for removing the adsorbate before they leave the column (transportation of adsorbate into the immobile phase).
 - i) Liquid phase or external mass transfer. This mechanism is characterized by the external mass transfer coefficient (K_p), and can be estimated through the correlation proposed by Gnielinski (1974).
 - ii) Local adsorption equilibrium at the surface of the adsorbent. If multi-organic compounds are present,

competitive equilibrium of adsorbates upon the adsorbent surface should be considered (Radke and Prausnitz, 1972). Equilibrium or capacity parameters such as Freundlich K & $1/n$ for these various organic compounds have to be evaluated (Randtke and Snoeyink, 1983) to describe this phenomenon.

- iii) Intra-aggregate mass transfer, either through surface diffusion or pore diffusion or both.

Hence it is clear that to properly describe the GAC adsorption process, it is essential to quantify the adsorbate mass transfer and adsorption equilibrium mechanisms. These mechanisms in-turn are influenced by the following two factors:

- 1) Competitive interactions among the various adsorbates, reduces the effective adsorption capacity of a target compound in the presence of other organic compounds (Radke and Prausnitz, 1972). Competition may also reduce the kinetics of mass transfer of a target compound onto the immobile phase, due to adsorbate-adsorbate interactions during the diffusion process.
- 2) The uncharacterized background organic matter (BOM) present in water, influences both the adsorption capacity and kinetics of the target compound by a process known as "pre-loading" or "fouling" of GAC (Zimmer, 1988). BOM usually is at a higher concentration than the SOCs, and has a slower adsorption kinetics and less adsorption capacity for GAC. Consequently, BOM moves rapidly through the bed due to its larger mass transfer zone. As a result, GAC deeper in the bed is exposed to BOM before the arrival of SOCs. The adsorbed BOM (due to its polymeric structure) covers the adsorbent surface and blocks the pores of the adsorbent, and is difficult to be dislodged because of its multiple attachment sites between the GAC and BOM, thereby reducing the capacity and kinetics of adsorption of target compound.

Once the most significant of the above two factors is determined for a particular field condition, it is possible to evaluate its impact on the adsorption capacity and kinetics for a target compound.

Selection of design parameters

It is imperative that initially, identification of target compound(s) and its/their treatment objectives (TO) be carried out before selecting the optimum design parameters of the GAC adsorber. Target compound(s) should be chosen based on the following considerations.

- 1) The weakly adsorbing adsorbates that are liable to breakthrough from the adsorber at the earliest. This early breakthrough potential depends upon the organic chemicals' concentration as well as their adsorption capacity.
- 2) Target compounds should be so chosen, only if they are to be regulated. Supposing an organic chemical that is not regulated is identified as the chemical that will breakthrough early from the adsorber, still it should not be chosen as a design target chemical.

Once the decision about design target chemicals are made, then steps should be taken to determine the actor controlling the adsorption process (i.e. multi-adsorbate competition vs. BOM fouling). This can be evaluated by means of a lab-scale column experiments to evaluate the breakthrough profiles of known SOCs and uncharacterized BOM (measured through a surrogate parameter such as TOC). A simpler quantitative method proposed by Bhuvendralingam (1992) can also be used for this purpose in the absence of lab-scale column data.

Once the above mentioned identification is made, estimation of design parameters should be carried out such that the treatment cost is minimized. Typical adsorber design parameters are namely: type of GAC, GAC particle size, empty bed contact time (EBCT), and bed operation/configuration (beds in series or parallel beds).

If the adsorption process is controlled by multi-adsorbate competition, then particular care should be given in estimating the following design parameters.

- 1) GAC particle size: Smaller particle sizes promotes increased kinetics. But if the particles become very small, such as powdered activated carbon (PAC), then it could not be used in fixed-bed applications.
- 2) Type of GAC: GAC with appropriate pore size distribution suitable for the removal of identified target compound should be selected. Pore size distribution of GAC can be controlled by the degree of activation and choice of base materials (bitumen, wood, coconut etc.)
- 3) EBCT: Adsorbers with larger EBCT will yield larger specific throughput (volume of water treated per unit mass of GAC). This is because the ratio of length of active mass transfer zone to the length of the column decreases with increasing column length.
- 4) Bed configuration: The choice of bed configuration depends on the level of TO. For a strict TO (where $C_{TO} < 0.05 C_o$), beds-in-series option would provide the best results. For a more relaxed TO (where $0.05 C_o < C_{TO} < 0.4 C_o$), parallel bed option would provide the best results (Crittenden *et al.*, 1987). Please note that C_o refers to influent concentration.

If the adsorption process is controlled by GAC fouling, then following considerations should be given to the process design.

- 1) Type of adsorbent: Adsorbents other than GAC may be used in this instance. Macro-reticular resins (Rohm

and Haas, PA) and molecular sieves (Union Carbide, CA) which have been shown to be resistant to BOM fouling may in the long run prove to be economical, though they are more expensive than GAC.

- 2) EBCT: Though adsorbers will yield increasing specific throughput with EBCT when the adsorption process is controlled by competition, the specific throughput will start to decrease after the adsorber exceeds a critical EBCT due to the fouling impact of BOM. For most practical cases, an adsorber with an EBCT of 9 to 15 minutes will yield the largest specific throughput.

- 3) Bed Configuration: In this situation, beds-in-series operation would yield the highest specific throughput irrespective of the treatment objective. It has been found that using 2 adsorbers in series with the total EBCT in the same range will treat about 35% more water (Sontheimer *et al.*, 1988).

Current developments

Two of the current developments that look promising in this field are:

- 1) Operating the adsorber on a layered upflow carbon adsorption (LUCA) mode (Munz *et al.*, 1990). During LUCA operation, GAC is added in thin layers, with a new layer being added whenever TO of the contaminant is reached. Thus, the time of exposure of GAC to BOM, which is known to foul GAC's adsorption capacity for organic contaminants is reduced. This mode of operation was found to produce 50% of higher throughput.
- 2) A process known as "phase-transfer advanced oxidation" has been found to be a feasible option to regenerate the carbon without taking the adsorber out of service. This process consists of 2 consecutive operational steps: (1) fixed-bed adsorption using GAC and (2) destructive regeneration using impregnated photocatalyst such as titanium dioxide (TiO_2). Depending on the UV-light intensity and impregnation dosage, regeneration time was found to be in the range of 1/5 to 2 of adsorption time (Notthakun, 1991). About 5% of virgin capacity was found to be successively lost through each regeneration cycle. This loss was attributed to the build-up of surface oxides on the GAC.

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