# Organic matter removal via activated sludge immobilized gravel in fixed bed reactor

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**Abstract.** In this study, the adsorption capability of the activated sludge immobilized gravel as a low-cost and efficient adsorbent to remove organic matter in terms of chemical oxygen demand (COD) from synthetic wastewater was investigated using fixed bed columns. The effects of parameters including column pack height and influent COD concentrations on removal efficiencies were assessed through breakthrough curves. It was found that the removal efficiency increased when fixed bed height was increased and influent COD concentration was decreased. The maximum COD removal rate of 36.35%, was obtained for a medium-strength wastewater sample with 1166 mg/L of COD concentration when the bed height was 2 cm, and the flow rate was 11 mL/min. Activated sludge immobilized gravel can be utilized as a low cost bio-filter to remove organic material from wastewater.

## 1 Introduction

The concentration of organic pollutants is the main parameter to describe the strength of the wastewater. Industrial and municipal wastewater contain a variety of organic compounds. Illegal dumping and ineffectively treated wastewater effluents can cause pollution to the receiving bodies in the environment. Therefore, unconventional low-cost treatment systems are attracting more attention because of their ability to effectively remove organics from wastewater[1].

Gravel is one of the natural materials that has been underutilized even though it exhibited potentials to be a low-cost, effective adsorbent in wastewater treatment. Several studies have shown that gravel exhibited high adsorption capacities towards nitrogen, phosphorus, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC),metal ions, and some bacteria [2-6]. The biodegradation is suggested as a low-cost and efficient technique to degrade the organic pollutants from wastewater [5, 7-12]. Among different biologic treatment systems, biofilter/biorector systems utilizing immobilization of microorganism on different media were studied extensively to remove phenol, chlorophenol, dichlorophenol, quinoline, phthalic acid esters, nitrogen, heavy metals, and azo dye [13-19]. Experimental studies showed that immobilized microorganisms in a bioreactor showed higher removal rates when compared to conventional suspended systems. A tubular packed bed bioreactor with immobilized activated sludge culture showed 90% of COD removal from wastewater [20]. Another study reported formaldehyde degradation in a bioreactor with pumice stone as a support, and showed 97.1% of formaldehyde and 88% of COD removal efficiencies on average [21]. Surfactant-modified zeolites having a range of sizes from 0.25 mm to 0.5 mm removed phosphorus between 3.56% to 65% efficiencies when immobilized with orthophosphate accumulating bacteria [22].

A good carrier for the immobilization should be insoluble and stable in water, easily accessible, low-cost and non-toxic to microorganism [19]. In this respect, in this study gravel as a low-cost adsorbent was chosen as carrier for immobilization of activated sludge. Accordingly, activated sludge immobilized gravel (GAS) was evaluated to remove organic matter in terms of COD from wastewater in fixed bed reactor. COD is a measurement of the oxygen required to oxidize organic matter in water [23] . The effects of parameters including column pack height and influent COD concentration on the effluent COD concentration were investigated using breakthrough curves.

## 2 Materials and Methods

### 2.1 Filter media preparation

The gravel in the fixed bed columns were composed of particle with the diameters of 2.38-2.8 mm. It was characterized with a variety of analytical and spectroscopic techniques including scanning electron microscope (SEM), energy-dispersive X-ray (EDX), X-Ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) surface area analysis. The results of the

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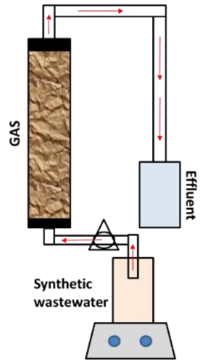
characterization were published elsewhere [24, 25]. The immobilization of the activated sludge on gravel was verified with SEM using JSM-7610F. The gravel was coated with platinum by an auto fine coater, JEOL JEC-3000FC, in 40 second and at 40 Pa for SEM images.

### 2.2 Synthetic wastewater preparation

An established **protocol** was adopted to prepare the synthetic wastewater samples [24-27]. All the measurements were run at pH 7 adjusted by using NaOH or HCl solutions. The effect of wastewater concentration on the adsorption efficiency was analyzed by changing the strength of the wastewater. The initial synthetic wastewater solution was termed as strong 1X wastewater, and found to have 3575 $\pm$ 131.52 mg/L of COD. 0.5X synthetic wastewater was found to contain 1166 mg/L of COD. All chemicals were analytical reagent grade and obtained from Fisher Scientific and Sigma Aldrich. Influent and effluent COD concentrations were determined using Hach LCK 314 COD vials which were digested in Hach DRB200 digital thermostat reactor and measured in Hach DR6000 UV-visible spectrophotometer. A Hach multi-meter HQD4D was used to measure the pH.

### 2.3 Immobilization of activated sludge culture on gravel and fixed bed operation

An activated sludge sample as microbial immobilization culture was obtained from the second clarifier of a local wastewater treatment plant in Abu Dhabi/UAE. The activated sludge was transferred to a laboratory scale aeration tank and kept at 24 $^{o}$C with dissolved oxygen (DO) amount of 7$\pm$ 1 mg/L and fed by synthetic feeding solution. The protocol for the preparation of synthetic feeding solution was adopted from a previous study [28]. Activate sludge culture containing 1063$\pm$150 mg/L mixed liquor suspended solids (MLSS) was recirculated by a peristaltic pump (Welch Model 3200) through the duplicates of columns having 8 cm height and 1.6 cm inner diameter at 11ml/min flow rate for the immobilization on gravel as shown in Figure 1. The culture solution was replaced daily for 7 days for full immobilization. The immobilization of the microorganism was observed visually as well as with SEM. Activated sludge immobilized gravel was named as GAS. After 7 days, column media was covered with sludge, and the continuous column study was started. Synthetic wastewater solutions were stirred using a magnetic stirrer and pumped in upward direction in the columns by a peristaltic pump. The pH of the samples was adjusted to 7 to mimic the pH of the municipal wastewater. Effluent samples were collected at different times, then filtered using 0.45 µm syringe filter, and analyzed with the UV-VIS spectrophotometer.




(b)

**Fig 1**. Column set up for activated sludge immobilized gravel (GAS)

Wastewater flow was terminated at time t when the concentration of a COD in the effluent was found to reach 98% of its initial concentration based on the formula $C_t$= 0.98x$C_o$ where $C_t$ is the COD concentration at time t, and $C_o$ is the initial COD concentration in the wastewater sample.

The total adsorbed organic materials, $q_{total}$ (mg), is equal to the area under the curve for the concentration of adsorbed organic, $C_{ad}$ ($C_{ad}$=$C_0$–$C_t$) (mg/L) over the time, t (min) using Eq. (1):

$$q_{total\,(mg)} = \frac{Q.A}{100} = \frac{Q}{1000}\int_0^{t_{total}} C_{ad}dt \qquad (1)$$

where Q is the volumetric flow rate (mL/min). The dynamic adsorption capacity, $q_e$ (mg/g), was calculated using Eq (2):

$$q_e = \frac{q_{total}}{m} \qquad (2)$$

where m is the mass of adsorbent (g). The removal efficiency of organic matter is the ratio of total adsorbed organic matter in the column to the total amount of organic matter found in the influent according to Eq. (3):

$$Efficiency = \frac{q_{total}}{C_o\frac{Q}{1000}t_{total}}x100 \qquad (3)$$

The column adsorption capacities were calculated based on the Thomas model according to Eq(4):

$$Ln\left(\frac{C_0}{C_t} - 1\right) = k_{Th}q_0\frac{m}{Q} - k_{Th}C_0t \qquad (4)$$

where $k_{th}$ is the Thomas rate constant (L/mg.h), $q_0$ is the Thomas column adsorption capacity (mg/g) and t is the filtration time (min). The linear graphs of ln [$(C_0/C_t)$−1] against $t$ were plotted to derive the values of $k_{th}$ which correspond to the slope and $q_0$ which corresponds to the intercepts.

## 3 Results

### 3.1 SEM results

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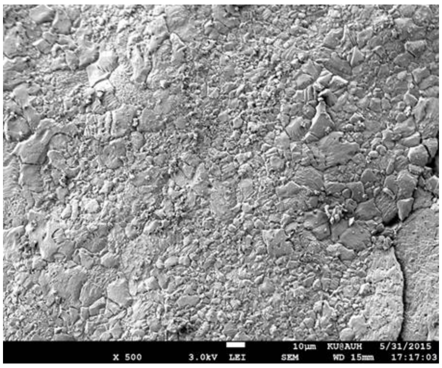
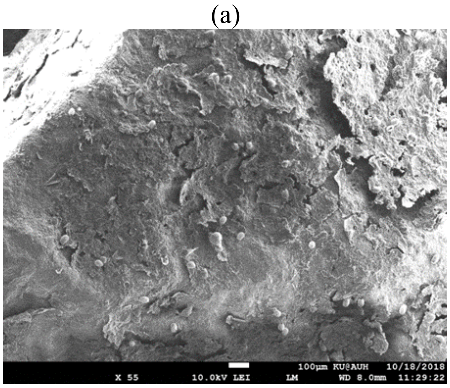
Immobilization on gravel was verified using SEM imagining. The SEM image revealed roughness on the surface of the gravel before immobilization as shown in Figure 2a, and the efficient immobilization of the microorganisms on the gravel as shown in Figure 2b. Microorganisms colonized macro pores and crevices of the gravel and resulted as a biofilm.




(a)




(b)

**Fig 2**. SEM images of (a) gravel at 500 X (b) activated sludge immobilized gravel (GAS) at 500 X

### 3.1 Fixed-bed column experiments

The effect of the initial wastewater strength on the adsorption of the organic matter by GAS in the fixed bed column study was presented as Ct/Co per day shown in Figure 3. Higher removal efficiency was obtained for 0.5X wastewater in columns with a bed height of 2 cm. The average COD removal efficiency was 36.35% for 0.5X wastewater, whereas the COD removal efficiency decreased to 15.5 % with 1X wastewater. This indicates that organic compounds saturate the binding sites immediately, and the performance deteriorates accordingly [27]. The total adsorbed COD was high for systems with high inlet COD concentration as shown in Table 1. The adsorption process is driven mainly by the concentration gradient between adsorbent and solution. A high solute concentration in solution provides a strong stimulus for the efficient adsorption process, and this explains higher adsorption efficiencies towards samples with high COD concentrations [29].

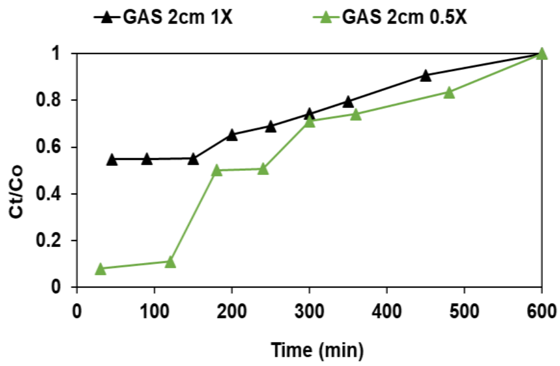



**Fig 3.** Breakthrough curves for 0.5X or 1X wastewater samples obtained for columns with 2 cm bed heights

**Table 1.** Exhaustion times, % removals, and dynamic adsorption capacities

| Condition | $q_e$ (mg/g) | $t_e$ (min) | % Removal |
|---|---|---|---|
| **2 cm 1X wastewater** | 629.254 | 600 | 15.5 |
| **2 cm 0.5 X wastewater** | 588.126 | 600 | 36.35 |
| **4 cm 1X wastewater** | 1125.419 | 1050 | 20.66 |

It was noted that the volume of treated wastewater as well as the amount of adsorbed organic matter increased as the bed height increased. The average COD removal efficiency was 20.66% for 1X wastewater in columns with 4 cm bed height and 15.5 % for 1X wastewater in columns with 2cm bed height as shown in Figure 4. The higher the bed height was, the more the binding sites were available. The overall time to exhaust the column was found to be more for 4 cm bed height in GAS fixed bed columns. In this manner, columns with longer bed heights could operate in longer periods. In contrast, the exhaustion occurred faster with the shorter bed heights, therefore, the performance declined [30]. The amount of total adsorbed COD increased with the increasing bed height as shown in Table 2. Similar observations have been reported by other researchers [27, 31].

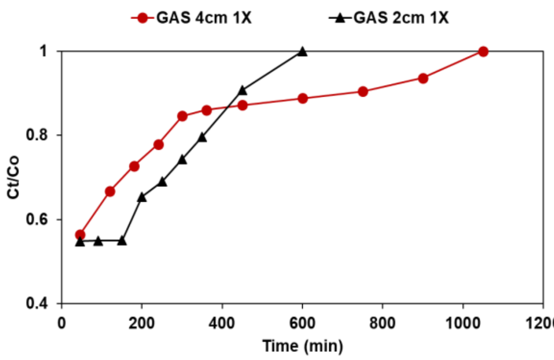



**Fig 4.** Breakthrough curves for 1X wastewater samples obtained for columns with 2 cm and 4 cm bed heights

Some other studies reporting microorganism immobilized on different carriers showed higher COD removals than our study findings. For instance, the bacterium isolated from the wastewater was immobilized onto a new type of ceramic carrier by a vacuum method, and the resulting system removed more than 82% of the influent COD [32]. Another study revealed that, a pilot-scale zeolite medium biological aerated filter was able to remove 73.9% of COD for a sample with an initial concentration of 400 mg/L COD [33]. Lower COD removal rates in this study might stem from the choice of gravel as a carrier. According to another study, the number of immobilized cells decreased with an increase in the particle size of the carrier [34]. Another factor which might contribute to the lower removal efficiency of COD in this study could be use of high initial COD concentration which could decrease the removal percentage.

The breakthrough curves of COD for the wastewater samples using fixed bed columns were plotted, and the resulting data was described with the Thomas model. The values of $q_0$ and $k_{th}$ indicating the performance of column were calculated. The GAS exhibited high-loading capacities for organic matters in fixed bed columns, and the uptake rate ranged from 785 mg/g to 1293 mg/g of COD according to Table 2. The correlation coefficients were between 0.91 to 0.99 indicating that Thomas model satisfactorily describes GAS adsorption capacities.

**Table 2.** Calculated values of $q_0$ and $k_{th}$ using Thomas model and corresponding $R^2$ values

| Conditions | $Q_o$ (mg/g) | $k_{th}$ (L/mg.h) | $R^2$ |
|---|---|---|---|
| **2 cm 1X wastewater** | 785 | $7.6 \times 10^{-5}$ | 0.99 |
| **2 cm 0.5 X wastewater** | 704.16 | 0.000625 | 0.91 |
| **4 cm 1X wastewater** | 1292.53 | $4.55 \times 10^{-5}$ | 0.92 |

The results shown in Table 3 clearly demonstrate the correlation between experimental results and Thomas model.

**Table 3.** Adsorption capacities of GAS obtained with experimental results and Thomas model

| Conditions | $q_o$ (mg/g) | $q_e$ (mg/g) |
|---|---|---|
| **2 cm 1X wastewater** | 785 | 588.126 |
| **2 cm 0.5 X wastewater** | 704.16 | 629.254 |
| **4 cm 1X wastewater** | 1292.53 | 1125.419 |

## 4. Conclusion

The efficiency of activated sludge immobilized gravel in fixed bed columns was tested to treat high and medium strength wastewater samples in order to remove organic matter. It was deduced that lower COD inlet concentrations and higher bed heights improved the removal efficiencies of columns. The maximum COD removal rate of 36.35% was obtained for a medium-strength wastewater sample (0.5X wastewater) with 1166 mg/L of initial COD concentration when the bed height was 2 cm, and the flow rate was 11 mL/min. Activated sludge immobilized gravel as a low-cost medium can be utilized in bio-filters to remove organic content from wastewater efficiently.

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