

Phenolic wastewater treatment

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A simple experimental set-up was used to study the treatability aspect of phenolic wastewater. Three types of systems: i) Activated Sludge (A.S), ii) granular Activated Carbon (A.C) and iii) Activated Sludge plus Activated Carbon (A.S + A.C) were experimented under different phenol loadings (100, 200 and 300 mg/l) and different flow rates (21.6 and 43.2 l/d) with initial COD concentration 500 mg/l. Phenol toxic effect on biomass was also investigated. The A.S + A.C system gave the highest COD and phenol % removal comparing with the other two systems. Results showed that increasing phenol loading had an adverse effect on treatment efficiency for all cases. Respirometric analysis indicated that, for A.S system, μ^H decreased from 3.20 d⁻¹ at 0.0 mg/l phenol concentration to 2.26 d⁻¹ at 100 mg/l phenol concentration. Increasing phenol load to 300 mg/l results in decreasing μ^H to only 1.21 d⁻¹. In order to confirm these results, the toxic effect was measured by following the fraction of Specific Oxygen Uptake Rate (SOUR) loss between the sludge with zero phenol and the sludge dosed with phenol. Results obtained indicated an increasing of toxicity factor from 0.325 at phenol concentration of 100 mg/l to 0.63 at phenol concentration of 300 mg/l.

يهدف هذا البحث الى دراسة قابلية إزالة الفينول من المخلفات السائلة في ٣ أنواع من الأنظمة: حمأة منشطة، كربون منشط، حمأة منشطة مع كربون منشط. وقد أجريت التجارب العملية تحت تأثير تركيزات مختلفة من الفينول (١٠٠، ٢٠٠، ٣٠٠ مجم/لتر) و تصرفات متغيرة (٢١,٦ و ٤٣,٢ لتر/يوم) و كان تركيز COD الابتدائي ٥٠٠ مجم/لتر. و قد وجد أن نظام الحمأة المنشطة مع الكربون المنشط يعطي أعلى كفاءة في إزالة ال COD و الفينول مقارنة بالنظامين الآخرين. كما أتضح أن زيادة تركيز الفينول في المخلفات السائلة له تأثير سلبي على كفاءة المعالجة للأنظمة الثلاثة. و لدراسة التأثير السمي للفينول على البكتريا فقد تم قياس معدل نمو البكتريا في نظام الحمأة المنشطة و قد اتضح أن معدل نموها قد تناقص من ٣,٢٠ يوم^{-١} عند تركيز فينول صفر في المخلفات السائلة الى ٢,٢٦ يوم^{-١} عند تركيز فينول ١٠٠ مجم/لتر و الى ١,٢١ يوم^{-١} عند تركيز فينول ٣٠٠ مجم/لتر. من أجل التأكد من هذه النتائج فقد تم قياس معامل السمية باستخدام تعيين SOUR و قد اتضح أن معامل السمية قد ارتفع من ٠,٣٢٥ عند تركيز فينول ١٠٠ مجم/لتر الى ٠,٦٣ عند تركيز فينول ٣٠٠ مجم/لتر.

Keywords: Industrial wastewater, Activated sludge, Activated carbon, Phenol, Toxicity, Oxygen uptake rate

1. Introduction

Phenol is an inhibitory and toxic compound present in wastewater from petroleum refining, petrochemical, coke conversion and pharmaceutical plants. Biological degradation of phenolic wastewater has been documented by several authors [1].

In the majority of the literature reports, the general consensus is that although phenols can be degraded in the activated sludge process, the presence of phenol in wastewaters increases the susceptibility of a biological system to become upset [2].

Although inhibitory and toxic, phenol is also a carbon and energy source for some microorganisms, there is scant data on the

biodegradation of high strength phenolic wastewater, which can exceed 1000 mg/l [2].

Paulowsky and [3] found the maximum specific growth rates of a mixed cultures grown on phenol as the sole carbon occurred at a substrate concentration of less than 100 mg/l. The steady-state phenol removal from a continuous flow of reactor reached 90%.

In addition to biological degradation, adsorption process, and in particular those using activated carbon, are finding increased use in wastewater treatment for phenol removal. Adsorption on Granular Activated Carbon (GAC) is one of the best commercial proven methods for removing toxic organic chemicals, such as phenol, from wastewater [4].

Addition of activated carbon to the aeration tanks suspended growth has been used to improve activated sludge operation and performance. A study by [4] indicated that activated carbon addition to activated sludge systems provides exceptional resistance to shock loading by phenol, presumably due to large reservoir of carbon.

A fixed-bed column is used commonly for contacting wastewater with GAC. Fixed-bed columns can be operated singly, in series, or in parallel. The water to be treated is applied to the top of the column and withdrawn at the bottom. The advantage of a downflow design is that adsorption of organics and filtration of suspended solids are accomplished in a single step [5].

The aim of this research to investigate the treatability aspect of phenolic wastewater. Three types of systems: i) Activated Sludge (A.S), ii) granular Activated Carbon (A.C) and iii) A.S + A.C were experimented under different phenol loadings (100, 200 and 300 mg/l) and different flow rates (21.6 and 43.2 l/d) with initial COD concentration 500 mg/l. Phenol toxic effect on biomass was also investigated.

2. Materials and methods

2.1. Activated sludge system

The activated sludge system consists of a reactor and a final settling tank. The synthetic sewage was introduced into the aeration tank with 43.2 l/d. A completely mixed Plexiglas reactor was assembled with 40 l aeration tank (surface area 99 cm²) connected by a silicon rubber tube to a 13.5 l settling tank having surface area of 525 cm². Variable speed peristaltic pumps (Master flex L/S Easy-Load) were utilized to recycle settled sludge and to feed the solution to the aeration tank. Aeration was supplied through diffusers located at the bottom of the aeration tank, supplied diffused air (approximately 2 mg/l level of dissolved oxygen) and maintained complete mixing. As shown in fig. 1.

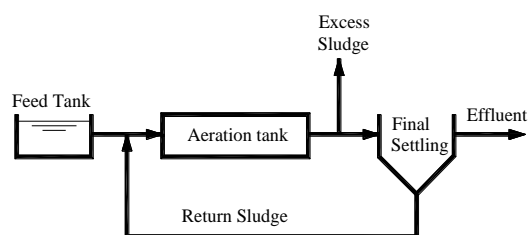


Fig. 1. Activated sludge system.

Initially, the activated sludge system was seeded with sludge from sequencing batch reactor treatment plant Mobarak wastewater treatment plant). The waste sludge was collected from the aeration tank. During start-up period the unit was fed with synthetic sewage and all settled sludge in the final settler was returned into the aeration tank. The start-up period was 14 days; steady-state condition was considered achieved by constant measured parameters of the effluent and Mixed Liquor Suspended Solids (MLSS) in the reactor. After reaching steady-state conditions, the laboratory unit was operated at sludge age of 10 days, the sludge was wasted directly from the aeration tank. During steady-state period F/M ratio ranged between 0.2 to 0.23 d⁻¹ with an average of 0.21d⁻¹, the MLSS ranged between 2318 to 2753 mg/l, and the effluent COD ranged between 45 to 70 mg/l with an average value of 55 mg/l.

2.2. Granular activated carbon system

To achieve the objectives of this work a perspex column with internal diameter 5 cm and 100 cm long were used. The column was packed with Granular active carbon [AquaSorb™2000]. Feed tank was made from plastic with capacity of 100 liters. The system was provided with a peristaltic pump which was designed for research purpose. The peristaltic pump was (Master flex L/S Easy-Load) and the pump was used as feeding pump. Collecting tanks were made from plastic with capacity of 50 liters. As shown in fig. 2.

2.3. Activated sludge plus activated carbon system

The experimental work was conducted by operating activated sludge pilot plant followed by activated carbon system, as shown in fig. 3.

2.4. Synthetic sewage

According to [6], the activated sludge process utilizing a synthetic sewage as prepared by diluting with tap water (1-100) a concentrated stock solution containing 48.6 g/l of glucose, 11.65 g/l of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and 8.8 g/l of $(\text{NH}_4)_2\text{SO}_4$. The synthetic sewage was daily prepared fresh. The diluted solution has average COD concentration equals to 500 mg/l.

2.5. Analytical techniques

Parameters monitored during this study were chosen to determine the system performance due to phenol loadings. Phenol concentrations was determined with 4-aminoantipyrine method. COD was measured by colorimetric method using spectrophotometers (DR 100 colorimeter Hach). Oxygen Uptake Rate (OUR), Specific Oxygen Uptake RATE (SOUR) and all other parameters were measured according to the standard methods for examination of water and wastewater [7]. The maximum specific growth rate of heterotrophs (μ^H) was measured according to the method proposed by [8].

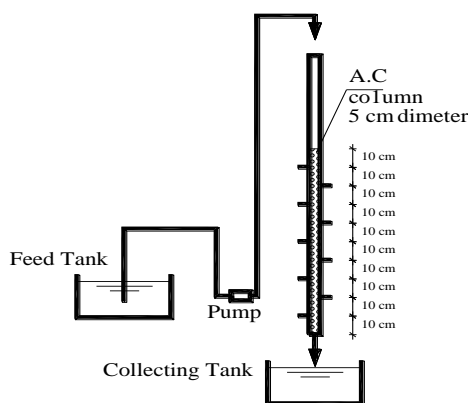


Fig. 2. Activated carbon column system.

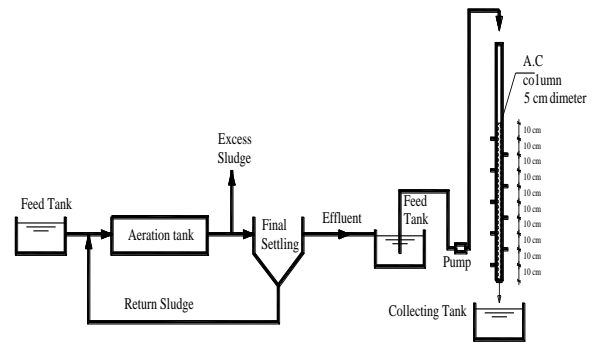


Fig. 3. Activated sludge and activated carbon column system.

3. Results and discussion

3.1. System efficiency

A comparison between the three systems regarding COD% removal is shown in fig. 4. for all cases , it is obvious that A.S + A.C system gave the highest COD% removal comparing with the other two systems. It is also clear that increasing operation time in all systems resulted in increasing the COD removal efficiency.

The adverse effect of phenol loading on COD removal can be recognized for all cases. For example, the average COD % removal was 84.80 % in A.S + A.C system after 14 days of operation with 100 mg/l phenol, adding 200 mg/l of phenol decreased the COD % removal to 77.2 %, while adding 300 mg/l of phenol decreased it to 62.3 %.

Fig. 5 shows a comparison between the three systems regarding phenol removal efficiency. From this figure, it is obvious that A.S + A.C system gave the highest % phenol removal. Also, increasing operation time in all systems resulted in increasing phenol removal efficiency.

Increasing phenol loading has an adverse effect on its removal efficiency. For example, after 14 days of operation the average phenol % removal decreased from 100 % in A.S + A.C system at 100 mg/l phenol to 95.9 % at phenol loading of 200 mg/l, and to 91.7% at phenol loading 300 mg/l for the same conditions.

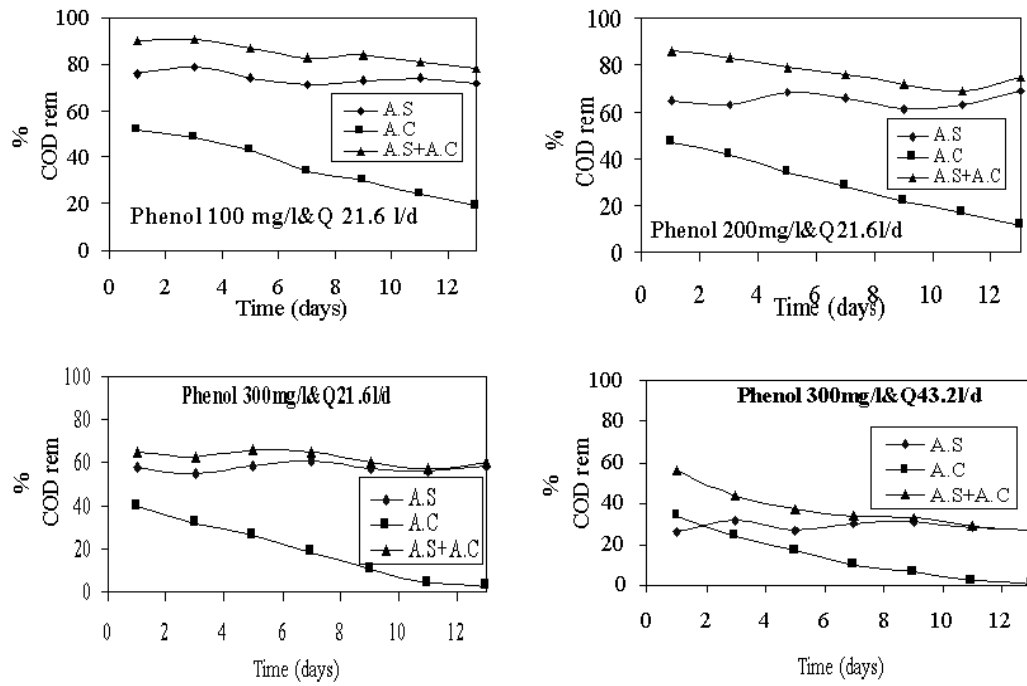


Fig. 4. Relation between % COD removal and the type of the system for different phenol concentrations and different flow rates.

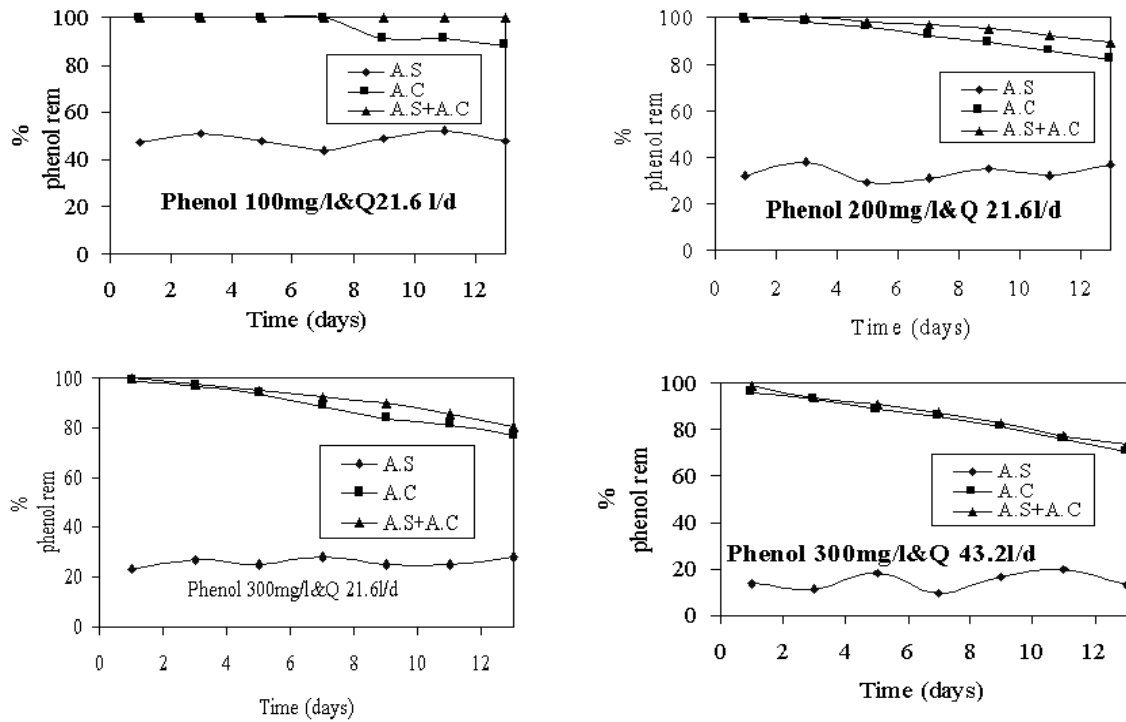


Fig. 5. Relation between % phenol removal and the type of the system for different phenol concentrations and different flow rates.

3.2. Phenol toxicity

Respirometric analyses were carried out to evaluate phenol toxic effect on biomass. These analyses were conducted on sludge of the A.S system. The toxicity effect on biomass was evaluated by measuring the maximum specific growth rate of heterotrophs (μ^H) for the batches at 0, 100, 200 and 300 mg/l phenol. The (μ^H) was estimated using the method proposed by [8]. They indicated that μ^H is usually specified as mg Active Volatile Suspended Solids (AVSS) synthesized per mg AVSS present per day i.e mg AVSS/mg AVSS/d or simply d^{-1} . It is related to the maximum readily biodegradable substrate utilization rate K_{ms} (in units mg COD/mg AVSS/d),

$$\mu^H = K_{ms} \cdot Y_h \quad (1)$$

Now K_{ms} (in mg COD/mg AVSS/d) is related to the initial high Oxygen Uptake Rate (OUR_i) at the beginning of the batch tests, OUR was measured after 10 min of operation and was repeated every 30 min. In general, for activated sludge process, carbonaceous removal is not only major sink for oxygen. In the presence of autotrophic microorganisms, nitrification also exerts a demand for oxygen.

$$K_{ms} = (1 / (1 - f_{ev} \cdot Y_h)) \cdot OUR_i \cdot ((V_{ww} + V_{ml}) / (f_{av} \cdot X_v \cdot V_{ml})) \quad (2)$$

Where:

f_{ev} is the COD/VSS ratio of the sludge (mg COD/mg VSS),

Y_h is the yield coefficient for heterotrophs (mg VSS/mg COD),

OUR_i is the initial high OUR in mg O_2 /l/d,

V_{ww} is the volume of wastewater in l,

V_{ml} is the volume of mixed liquor (at concentration X_v mg VSS/l),

f_{av} is the active fraction of the MLVSS, and

X_v is the MLVSS concentration of the mixed liquor added to the batch test mg VSS/l.

The toxic effect of phenol on biomass can easily be explained in fig. 6. The maximum specific growth rate μ^H was $3.20 d^{-1}$ at 0.0 mg/l phenol concentration, this value

decreased to $2.26 d^{-1}$ at 100 mg/l phenol concentration. Increasing phenol load to 300 mg/l results in a reduction of μ^H to $1.21 d^{-1}$.

No doubt that phenol toxicity has an adverse effect on heterotrophs growth rate, this should be considered in designing biological unit process for phenolic wastewater treatment. In order to confirm these results, the toxic effect of phenol on biomass was also evaluated using Specific Oxygen Uptake Rate (SOUR) measurements. SOUR has an interesting information capacity [6]. The toxic effect can be measured by following the fraction of SOUR loss between the sludge with zero phenol and the sludge dosed with phenol.

$$PT = 1 - SOUR^+ / SOUR^0 \quad (3)$$

Where:

PT is the phenol toxicity,

$SOUR^+$ is the specific oxygen uptake rate for sludge laden with phenol (mg O_2 /mg MLSS.h), and

$SOUR^0$ is the specific oxygen uptake rate for sludge with zero phenol (mg O_2 /mg MLSS.h).

The results obtained from SOUR measurements indicate an increasing of toxicity effect from 0.325 at phenol concentration of 100 mg/l to 0.53 at phenol concentration of 200 mg/l. Increasing phenol concentration to 300 mg/l resulted in increasing the phenol toxicity effect to 0.63. Fig. 6. Such results conform that increasing phenol loading results in increasing phenol toxicity and as a consequence decreases μ^H and activated sludge performance efficiency.

4. Conclusions

1. The A.S + A.C system gave the highest COD and phenol % removal comparing with the other two system (A.S and A.C systems).
2. Increasing the influent phenol concentration decreased the COD and phenol removal efficiency.
3. Increasing flow rate decreased the COD and phenol removal efficiency for all systems.
4. Increasing the influent phenol concentration results in decreasing the maximum specific growth rate of heterotrophs μ^H for A.S system.

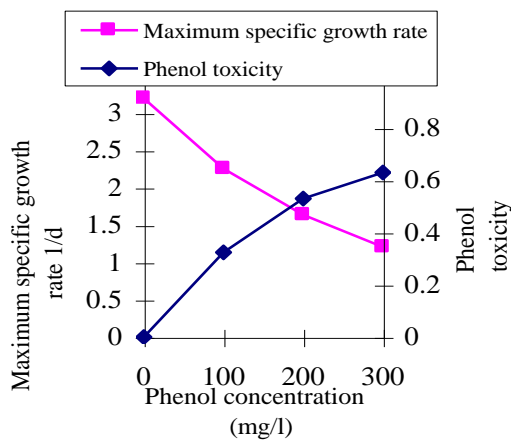


Fig. 6. Relation between maximum specific growth rate, phenol toxicity and phenol concentration.

5. Increasing the influent phenol concentration results in increasing phenol toxicity for A.S system.

List of abbreviations

- A.C is the granular active carbon [AquaSorb™2000],
- A.S is the activated sludge,
- COD is the chemical oxygen demand,
- f_{av} is the active fraction of the MLVSS,
- f_{ev} is the the COD/VSS ratio of the sludge (mg COD/mg VSS),
- F/M is the food to microorganisms (mg COD/day/mg MLSS),
- K_{ms} is the the maximum readily biodegradable substrate utilization rate (mg COD/mg AVSS/d),
- MLSS is the mixed liquor suspended solids,
- MLVSS is the mixed liquor volatile suspended solids,
- OUR is the oxygen uptake rate,
- OUR_i is the Initial oxygen uptake rate,
- PT is the phenol toxicity,
- $SOUR^+$ is the specific oxygen uptake rate for sludge laden with phenol (mg O₂/ mg MLSS.h)
- $SOUR^0$ is the specific oxygen uptake rate for sludge with zero phenol (mg O₂/mg MLSS.h),
- SS is the suspended solids,

- V_{ml} is the the volume of mixed liquor (at concentration X_v mg VSS/l),
- V_{ww} is the volume of wastewater in l,
- X_v is the MLVSS concentration of the mixed liquor added to the batch test mg VSS/l,
- Y_h is the yield coefficient for heterotrophs (mg VSS/mg COD), and
- μ^H is the maximum specific growth rate of heterotrophs.

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