Removal of organic compounds from waste streams: a combined approach

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Abstract

A combination of factors, including costs associated with wastewater treatment and more restrictive and stringent controls on industrial effluent pollution have increased interest in water usage reduction, recycling and re-use opportunities. In this study a novel two-step approach to treatment of low concentrations of organic compounds in waste streams was investigated. Zeolite ZSM-5 was investigated with a view to examining its potential to function as both adsorbent and catalyst in the removal of aniline from aqueous solutions. The H-ZSM-5 zeolite was first loaded with copper before the aniline adsorption step. The aqueous stability of the exchanged copper on the zeolite was assessed as a function of solution pH. Minimum copper leaching was observed in the range pH 5 to pH 11 thus providing a stable working pH range for the 1.4Cu-ZSM-5 to function as an adsorbent material. Aniline adsorption was then carried out and an uptake level of 40 mg g^{-1} aniline on the 1.4Cu-ZSM-5 zeolite was achieved. The adsorption process followed the Langmuir model and aniline uptake was largely uninfluenced by temperature. The kinetics of the adsorption process indicated that maximum uptake of aniline occurred within thirty minutes. In the second step of the process, the aniline loaded Cu-ZSM-5 adsorbent samples were subjected to a catalytic oxidation process and mass spectroscopic analysis of the catalytic reactor exhaust gases suggested clear oxidation of the aniline to carbon dioxide, water and nitrogen, with minor amounts of nitrogen oxide gases being produced.
Keywords: organics, ZSM-5, adsorption, catalytic oxidation, waste stream treatment.

1   Introduction

Water plays an integral role in both domestic and industrial life. The UN estimates that by the middle of this century, at best, 2 billion people in forty eight countries will experience water scarcity, i.e. their annual fresh water resources will be less than 1000m^3 per capita per year. At worst, 7 billion people in sixty countries will experience severe water shortage [1]. In industry, new, innovative and cost-effective technologies are necessary to develop the recycling and reuse potential of industrial process waste streams. Examples of industries with significant water usage and potential for treatment and recycling include the pharmaceutical, refining, food and beverage, chemical, petrochemical, pulp and paper and electronics sectors [2]. In general the reduction of wastewater in any given industry can be achieved in a number of ways including process modification, changes in raw materials used or water consumption reduction programmes [3, 4]. In practice, significant waste stream volumes are produced and where feasible the recycling and regeneration of these streams is of significant environmental and economic benefit.

A number of well-established technologies exist for waste stream treatment and recycling, including reverse osmosis (RO), micro filtration (MF) and ultra filtration (UF) [2, 5]. Alternatives for treating waste streams containing organic type impurities include specific oxidation methods which can be divided into the following categories: chemical oxidation and air/oxygen based catalytic (or non-catalytic) oxidation. The former category includes advanced oxidation processes (AOPs). Typical AOPs use ozone, hydrogen peroxide and UV radiation to generate hydroxyl radicals used for oxidation [6]. However, these processes tend to be limited by their intensive costs. The latter category includes dry oxidation, wet air oxidation and catalytic wet air oxidation.

Currently, there is a strong interest in developing alternative adsorbents for the removal of organic pollutants from aqueous waste streams. Zeolites are one type of alternative adsorbent material and have the ability to selectively adsorb or reject molecules based upon molecular size, shape and other properties including polarity. To date, limited studies have been carried out on zeolite adsorption of organic molecules from aqueous solutions [7–9]. Zeolites also have the ability to function as catalysts. In this work ZSM-5 zeolite is loaded with copper to promote and enhance its catalytic activity. Copper exchanged zeolites have been shown to be extremely active for the catalytic oxidation of ammonia, to nitrogen and water with low levels of NO and N$_2$O formed [10]. Centi and Perathoner [11] studied the adsorption and subsequent wet and dry oxidation of low levels of sodium gluconate and triethanolamine onto a series of mixed oxides. Our present work sets out to build on this knowledge.

The aqueous contaminant of interest (aniline) is chosen as the test compound as it is a nitrogen-containing hydrocarbon typical of compounds occurring in waste streams from dye, pigments, pharmaceuticals, rubber additives and pesticides manufacture. It will firstly be removed by adsorption onto a selective adsorbent Cu-ZSM-5 zeolite and, secondly, oxidation of the adsorbed pollutant

into carbon dioxide, water and nitrogen with the simultaneous regeneration of the adsorbent/catalyst will be carried out (figure 1).
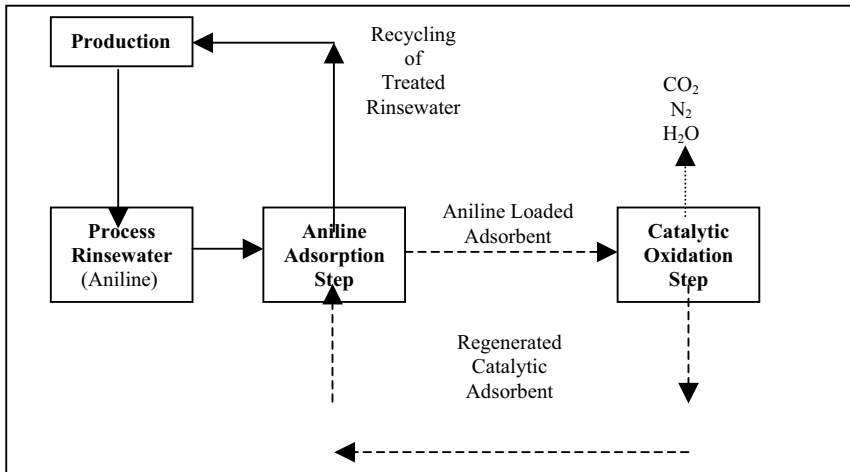

Figure 1:   Adsorption/catalytic process schematic for treating and recycling waste streams.

2   Methodology

2.1   Materials and zeolite characterisation

Copper exchanged ZSM-5 zeolites were prepared using a one step procedure similar to that reported by Iwamoto et al. [12]. Briefly, the appropriate amount of copper nitrate trihydrate (Aldrich) was dissolved in water and the zeolite ($SiO_2:Al_2O_3$ = 80:1) added to the aqueous salt solution. The suspension was stirred for 24 hours at room temperature and adjusted to pH 7.0 with a NH_4OH solution. The sample was filtered and dried at $80^{\circ}C$ for 10 hours, calcined at $450^{\circ}C$ for 5 hours and sieved to a particle size range of 212 - 850µm. A 1.4Cu-ZSM-5 indicates a zeolite containing 1.4wt% copper (measured by AA) on the ZSM-5 zeolite support prepared by ion exchange. Typically, 0.1g of the copper exchanged zeolite was dissolved in 3 mls of hydrofluoric acid and diluted for AAS analysis. The samples were characterized by nitrogen gas adsorption/desorption isotherms using a Micromeritics Gemini ASAP 2010 system. Samples were pretreated at 150°C for 17 hours and zeolite surface areas were measured using the Brunauer–Emmett–Teller (BET) method [13]. The zeolites were also characterised by X-ray diffraction using a Philips X'pert PRO MPD (multi purpose diffractometer) X-ray diffractometer PW3050/60 $\theta-\theta$ with a scan range of 5-60° (2θ) using nickel filtered Cu Kα radiation (λ = 1.542Å) at 40kV with a current of 35mA.

2.2 Copper leachability testing

The influence of aqueous solution pH on the possible leaching of the copper exchanged onto the ZSM-5 support was evaluated for solutions with initial pH between pH 1 and pH 11. Specifically, the pH of 150ml distilled water was adjusted appropriately using either HCl or ammonia solution (35% NH_3) and 0.5g of the copper exchanged adsorbent material was added to the solution. The solution was stirred continuously and samples were periodically withdrawn, vacuum filtered, centrifuged at 3,500 rpm and analysed by AAS.

2.3 Adsorption isotherms

An adsorption isotherm was prepared for aniline adsorption onto the 1.4Cu-ZSM-5 at 6°C and 24°C using a batch technique. The adsorbent, (0.1g), was allowed to reach equilibrium with aniline solutions (10ml) of known concentrations (50 and 4000 mg dm^{-3}). The solutions were stirred for one hour. The contents of each adsorption flask were then separated by centrifugation at 3,500 rpm for 20 min and filtered under vacuum. Pre and post-adsorption concentrations of aniline were determined by a Cary UV-Visible spectrometer (λ_{max} 230nm) and the amount adsorbed was calculated by the difference.

2.4 Catalytic oxidation experiments

The aniline loaded adsorbent/catalyst (100 mg) was placed in the quartz reactor and held in place by quartz wool plugs (figure 2). Before testing, the spent adsorbent sample was pre-treated for 60 minutes in a stream of a 3% oxygen-helium mixture at a flow rate of 50ml/min. The sample was then subjected to a temperature increase of 10°C/min up to 750°C. Products leaving the reactor in the exhaust gases were continuously monitored using the Mass Selective Detector (MSD).
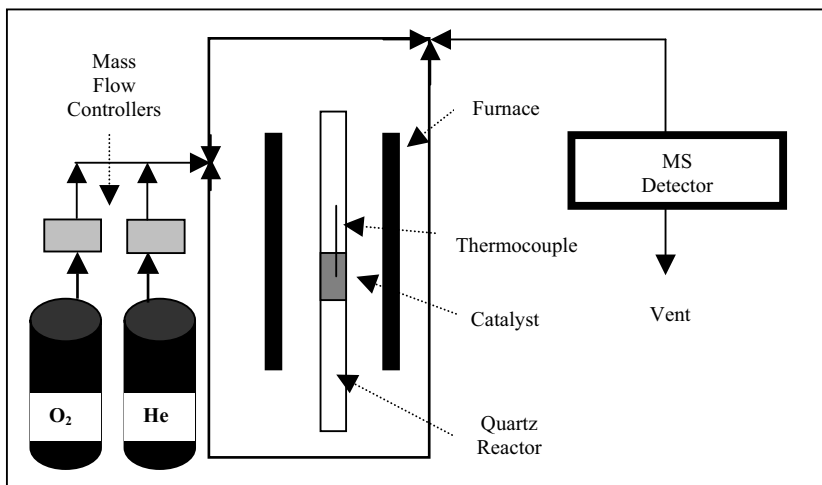

Figure 2:   Catalytic oxidation setup.

3   Results and discussion

3.1   Characterization

In this study, the actual copper loading on the zeolite was 1.4wt%, which corresponded to an ion-exchange level of 108%. This exchange level was based on the assumption that a single Cu^{2+} charge balanced a pair of negatively charged aluminium sites on the zeolite framework. The X-ray diffraction patterns of the copper-exchanged zeolite was identical to that of the parent zeolite indicating good dispersion of the copper on the catalyst and the absence of any crystalline copper phase. The surface area of the copper-exchanged ZSM-5 zeolite adsorbent was estimated to be 223 m^2g^{-1} as compared to 275 m^2g^{-1} for the unmodified H-ZSM-5.

3.2   Stability of the copper loaded ZSM-5 zeolite

Leaching tests were undertaken on the 1.4Cu-ZSM-5 sample in order to assess the extent of copper leaching as a function of aqueous pH. The results of this study are summarized in Table 1. From these results it is clear that the 1.4Cu-ZSM-5 material was most stable over the range pH 5 to pH 9, where the leached copper levels were less than 1 mg dm^{-3}. Complete copper leaching was calculated to give a resultant aqueous concentration of 46 mg dm^{-3}. At the acidic pH's copper leaching was rapid and in all cases maximum leaching occurred in less than 30 minutes. A study into successive copper leaching on the 1.4Cu-ZSM-5 samples showed that no subsequent leaching occurs after initial leaching. Therefore, the 1.4Cu-ZSM-5 zeolite can be used as a stable adsorbent material in the aqueous phase for the purposes of this work.

Table 1:   Leaching tests on 1.4Cu-ZSM-5 (pH range 1 – 11).

	1.4Cu-ZSM-5					
pH	1	3	5	7	9	11
Copper Leached (%)	80	21.4	0.3	<0.1	<0.1	1.5
Aqueous Cu^{2+} (mg dm^{-3})	37	9.8	0.14	<0.1	<0.1	0.7
Maximum Leaching (mins)	<20	<20	N/A	N/A	N/A	<20

3.3   Adsorption capacity of 1.4Cu-ZSM-5 for aniline

A preliminary test to establish the time to reach maximum adsorption revealed maximum uptake of aniline within 30-40 minutes of contact with the adsorbent material. The adsorption isotherms for aniline on 1.4Cu-ZSM-5 at 6°C and 24°C are displayed in Figure 3. All samples show maximum aniline adsorption of between 37 - 42 mg g^{-1} suggesting that at this level the zeolite is saturated. This significant level of uptake indicates that the pore diameters of the ZSM-5 zeolite facilitate removal of significant quantities of aniline from an aqueous environment. The level of aniline adsorbed onto the zeolite support was largely unaffected by a change in temperature.
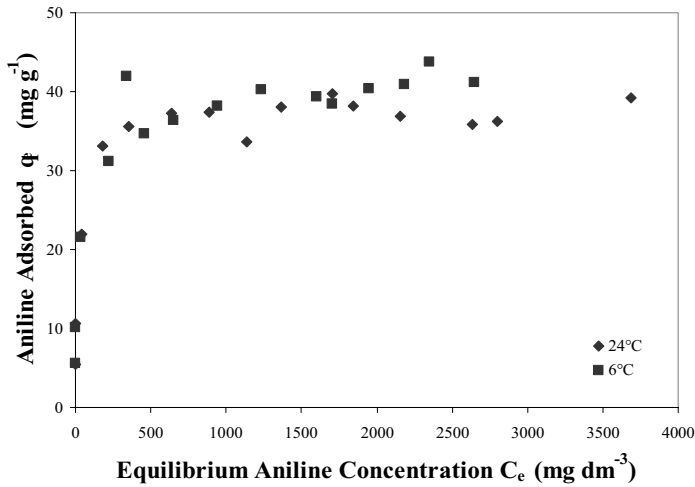
Figure 3:   Adsorption isotherm for aniline on 1.4Cu-ZSM-5 (■ 6°C, ♦ 24°C).

Table 2:   Langmuir constants for aniline adsorption on 1.4 Cu-ZSM-5 zeolite at 6°C and 24°C.

	1.4Cu-ZSM-5	Langmuir Constants		
Temp (^{o}C)	K_L ($dm^3 g^{-1}$)	A_L ($dm^3 mg^{-1}$)	K_L / A_L (mg g^{-1})	R^2
6	1.44	0.037	38.9	0.997
24	1.47	0.035	41.8	0.997

Both the Langmuir [14] and Freundlich [15] models, as defined below in Equations (1) and (2), respectively, were applied to the adsorption data.

$$q_e = \frac{K_L C_e}{1 + A_L C_e} \qquad (1)$$

$$q_e = K_F C^{1/n} \qquad (2)$$

where q_e is the amount of solute adsorbed per gram of adsorbent and K_L and A_L are Langmuir constants. A plot of C_e/q_e versus C_e from the linear form of Equation (1) was drawn to determine the values of K_L (intercept) and A_L/K_L (slope). Maximum uptake on the zeolite adsorbent surface was then obtained as K_L/A_L. The data in Table 2 indicate that the sorption of the aniline from aqueous solution onto the zeolite material showed good fit to the Langmuir model.

3.4 Kinetics and thermodynamics of aniline adsorption

Figure 3 suggests that temperature change from 6°C to 24°C has little impact on the aniline adsorption level. The results of the kinetic experiments undertaken on 1.4Cu-ZSM-5 are represented in Table 3.

Table 3:   Kinetic data displaying the equilibrium time required for aniline
adsorption at 24°C onto 1.4Cu-ZSM-5.

Initial Aniline Concentration (mg dm^{-3})	Maximum Adsorption Level (mg g^{-1})	Time to Maximum Adsorption (Minutes)
125	11	30
250	23	30
500	32	30

The findings revealed that equilibrium aniline uptake generally occurred within
approximately 30 minutes of contact time irrespective of the initial aniline
concentration used in the kinetic study.

3.5 Catalytic oxidation of adsorbed aniline

Figure 4 illustrates the desorption profile for aniline over H-ZSM-5 and 1.4Cu-
ZSM-5 during catalytic oxidation. The H-ZSM-5 sample was used to assess the
influence of copper loading on aniline oxidation. In the case of the H-Beta
zeolite, unreacted aniline is clearly visible in the exhaust gases from the reactor.
The presence of copper on the zeolite (1.4Cu-ZSM-5) considerably reduces the
concentration of aniline in the exhaust gases indicating strong oxidation of the
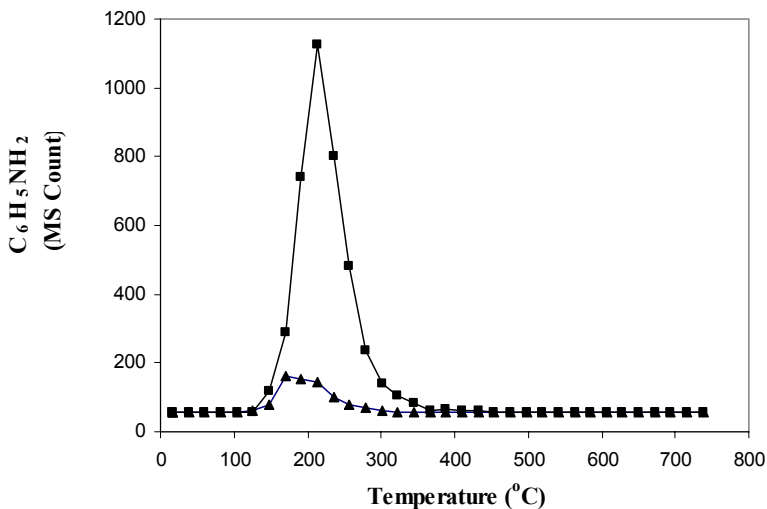adsorbed aniline to breakdown products.

Figure 4:   Comparison of the desorption of aniline on the ZSM-5 zeolites
(100mg of zeolite sample containing 10.5mg aniline, 3% O_2/He gas
flow, to 750°C at 10°C/min) (■ H-ZSM-5, ▲ 1.4Cu-ZSM-5).

The degradation of aniline sorbed on 1.4Cu-ZSM-5 should be accompanied by a corresponding increase in carbon dioxide level in the exhaust gases from the reactor as evidenced in figure 5. While aniline desorbs from the zeolite bed at 200°C, subsequent conversion into carbon dioxide does not occur until temperatures higher than approximately 400°C. Significantly, the CO_2 profiles in figure 5 also show that the presence of copper loading on the 1.4Cu-ZSM-5 zeolite effectively reduces the temperature required for oxidation of the aniline as evidenced by the lower temperature emission of CO_2. Preliminary work has also shown similar increases in nitrogen and water formation in the exhaust gases. Further work on the reproducibility of the 1.4Cu-ZSM-5 catalytic activity for aniline degradation over successive cycles is currently being researched.
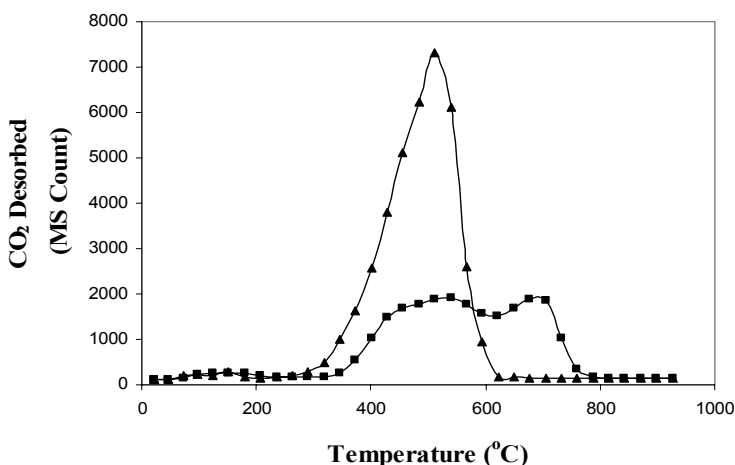

Figure 5: Comparison of the desorption of CO_2 on the ZSM-5 zeolites (100mg of zeolite sample containing 10.5mg aniline, 3% O_2/He gas flow, to 750°C at 10°C/min) (■ H-ZSM-5, ▲1.4Cu-ZSM-5).

4 Conclusion

A two-stage system was designed whereby initially the aniline was removed from solution by an adsorption step and subsequently the adsorbed aniline was catalytically oxidized to carbon dioxide, water and nitrogen with minor quantities of other gases. The 1.4Cu-ZSM-5 adsorption process (Step 1) has been shown to be effective with aniline uptake levels of 40 mg g^{-1} being achieved. The catalytic oxidation process (Step 2) has been shown to effectively destroy the aniline sorbed on 1.4Cu-ZSM-5. The system has shown considerable promise and further work is currently being carried out specifically to address a number of key issues including the suitability of the process for stripping other organic compounds, the potential selectivity towards specific organics, the mechanism by which the catalytic oxidation process occurs, potential de-activation of the

1.4Cu-ZSM-5 adsorbent/catalyst, the emission of carbon dioxide and the physical development of a larger scale system.

Acknowledgements

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