



A novel process for the removal of aniline from wastewaters

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ABSTRACT

The aim of this research was to develop a solid regenerable catalytic adsorbent capable of removing aniline from aqueous solutions. A H-Beta zeolite was first loaded with copper in an ion-exchange process to enhance its catalytic activity. Experimental results indicated an aniline adsorption level of approximately 106–114 mg g⁻¹ for each of the unmodified H-Beta, the 0.5% (w/w) Cu-Beta or the 1.4% (w/w) Cu-Beta zeolites. The adsorption processes followed the Langmuir model and the level of aniline adsorbed was largely unaffected by a change in temperature. Assessment of the aqueous stability of the exchanged copper on the Beta zeolites indicated minimum copper leaching in the range pH 5–11 thus providing a stable working pH range for both the 0.5% (w/w) and 1.4% (w/w) Cu-Beta adsorbent materials. Catalytic oxidation studies on the adsorbed aniline indicated that the presence of copper in the zeolites significantly enhanced the degradation of aniline to predominantly carbon dioxide, water and nitrogen. Five successive adsorption/catalytic oxidation cycles did not diminish the aniline adsorption capacity of the copper loaded zeolites but there was a small loss in the efficacy of the catalytic oxidation of the adsorbed aniline by the end of the 5th cycle.

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1. Introduction

In industry, the cost of water not only includes the direct cost but also costs incurred in bringing the water to certain specifications prior to use. Current and future legislation will lead to more stringent controls on industrial effluent pollution [1]. Industries such as the food and beverage industry, chemical, petrochemical, pharmaceutical and refining industries, pulp and paper industry and the electronics industry all generate large volumes of waste streams with significant potential for treatment and recycling [2]. In general, 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 leading to significant environmental and economic benefit [3,4].

Current technologies for waste stream treatment and recycling include membrane technology encompassing reverse osmosis (RO), micro filtration (MF) and ultra filtration (UF) [5–10]. Alternatives to membrane systems include oxidation methods based around chemical oxidation and air/oxygen based catalytic (or non-catalytic) oxidation. The first category includes advanced oxidation processes (AOPs) such as the use of ozone, hydrogen peroxide and UV radiation to generate hydroxyl radicals used for oxidation

[11–14]. These processes tend to be limited by their intensive costs. The second category includes dry oxidation, wet air oxidation and catalytic wet air oxidation [15–17].

Adsorption is another example of a physical treatment used in treating wastewater. Adsorption technology has been used for the removal of organics from wastewaters, primarily focusing on the use of activated carbon as the adsorbent of choice. Regeneration of the spent adsorbent material can be a costly and intensive process [18]. This has led to an interest in developing alternative adsorbents for the removal of organic pollutants from aqueous waste streams [19,20].

Zeolites have the ability to selectively adsorb or reject molecules based upon molecular size, shape and other properties including polarity and can therefore function as adsorbents. A number of studies outlining the adsorption of organic compounds from aqueous solution onto organo-clays [21], unmodified and modified zeolites [22,23], silicalite [24,25] and mesoporous materials [26] have been reported. Coupled with adsorbent characteristics, zeolites also have the ability to function as catalysts. Novel photocatalysts containing 2,4,6-triphenylthiapyrylium dye encapsulated within zeolite Y or Beta, or on amorphous silica or MCM-41 have been prepared for the adsorption and subsequent photocatalytic destruction of aniline and phenol [27]. The outcomes of the latter research work indicated that encapsulation of the dye within the pores of the zeolites increased the photostability of the dyes leading to higher organic adsorbate degradation productivity with successive runs possible but with a loss in photocatalytic activity

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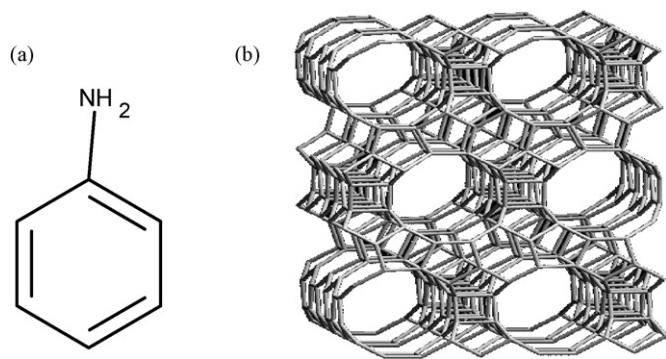


Fig. 1. (a) Chemical structure of aniline. (b) Chemical structure of zeolite Beta viewed along the [100] direction (Reproduced courtesy of Dr. Ch. Baerlocher, Laboratorium f. Kristallographie, Zurich, Switzerland).

with time. The loss of activity being attributable to pore blockage by the degradation products.

In this work Beta zeolite (Fig. 1(b)) 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 N₂O being formed [28]. Other research work has investigated the use of an activated carbon supported copper catalyst for the sorption and subsequent catalytic dry oxidation of phenol from solution [29]. Centi et al. studied the adsorption and subsequent wet and dry oxidation of low levels of sodium gluconate and triethanolamine onto a series of mixed oxides [30]. This present submitted work sets out to build on this knowledge.

Drawing on the potential combination of benefits from both adsorption and oxidation, the proposed system in this research work involves the development of a solid regenerable catalytic adsorbent for treating selected organic bearing wastewaters. This will be achieved by a two-step process involving, firstly, the removal of the aqueous contaminant, aniline (Fig. 1(a)), by adsorption onto a selective adsorbent Cu-Beta zeolite and, secondly, oxidation of the adsorbed pollutant into carbon dioxide, water and nitrogen with the simultaneous regeneration of the adsorbent/catalyst, whilst minimising the formation of nitrogen monoxide and nitrous oxide. Fig. 1(a) outlines the basic structure of aniline. It was chosen for use in this work because it is a simple nitrogen containing hydrocarbon representative of compounds typically occurring in waste streams. It is primarily employed in the manufacture of dyes, pigments, pharmaceuticals, rubber additives and pesticides [31].

2. Experimental

2.1. Materials

Copper-exchanged Beta zeolites (0.5% (w/w) and 1.4% (w/w) Cu-Beta) were prepared using a procedure outlined by Iwamoto et al. [32]. The appropriate mass of copper nitrate trihydrate (Aldrich) was dissolved in 500 ml distilled water and 10 g of the H-Beta (SiO₂:Al₂O₃ = 75:1) zeolite support (Zeolyst International) was added to the solution. The suspension was stirred for 24 h after which time the pH was adjusted to pH 7.0 using an 8.0% (v/v) NH₃ solution and the suspension stirred for a further hour. The sample was filtered and the filter cake washed. The filter cake was then dried and subsequently calcined at 450 °C in air for 5 h. Following calcination the unmodified and copper-exchanged Beta zeolites were sieved to a particle size range of 212–850 μm.

2.2. Zeolite characterisation

The copper modified zeolite samples (0.1 g) were dissolved in 3 ml HF and 10 ml distilled water and further diluted as appropriate. A Varian SpectraAA Atomic Absorption Spectrophotometer was used to determine the copper content of the metal exchanged zeolite. Characterisation of the sample was carried out by nitrogen gas adsorption/desorption isotherms using a Micromeritics Gemini ASAP 2010 system. The sample was pre-treated at 150 °C for 17 h before analysis. The apparent surface areas of the zeolites were measured using the Brunauer–Emmett–Teller (BET) method [33]. The zeolites were also characterised by X-ray diffraction using a Philips X'pert PRO MPD (multi purpose diffractometer) X-ray diffractometer PW3050/60 θ – θ with a scan range of 5–60° (2 θ) using a Cu K α line at 1.542 Å. A step size and scan speed of 0.017° (2 θ) and 0.2°/s, respectively were implemented. The Cu K α diffractometer anode was operated at 40 kV with a current of 35 mA.

2.3. Copper leachability testing

The leachability of the copper-exchanged onto the Beta zeolites was assessed over a range of pH conditions. The pH of 150 ml distilled water was adjusted appropriately using either hydrochloric acid or ammonia solution (35% NH₃) and 0.5 g of the copper-exchanged adsorbent materials was added to the solution. The solution was stirred continuously and samples were periodically withdrawn. The sample solutions were separated from the adsorbent material by vacuum filtration and the filtrate solution was centrifuged at 3500 rpm for 10 min and the supernatant was analysed for copper content by AA analysis using an air–acetylene flame and hollow cathode lamp wavelength of 324.7 nm.

2.4. Adsorption isotherms

An adsorption isotherm was prepared for aniline adsorption onto the H-Beta, 0.5% (w/w) and 1.4% (w/w) Cu-Beta samples at 6 and 24 °C using a batch technique. Accurately weighed amounts of each adsorbent were allowed to reach equilibrium with aniline solutions of known concentrations. Initial concentrations of aniline (maximum water solubility of 34 g dm⁻³) [34] were held between 50 and 3000 mg dm⁻³. This provided aniline aqueous solutions of pH range 6.6–7.0. Known weights of the zeolite materials (0.1 g) were added to glass vials, which contained 10 ml of solution. The solutions were stirred continuously for 1 h. The contents of the adsorption flask were then separated by centrifugation at 3500 rpm for 20 min and filtered under vacuum. Pre- and post-adsorption concentrations of aniline were determined spectrophotometrically (λ_{max} 230 nm) by a Varian (Cary) UV–visible spectrophotometer. The amount adsorbed was calculated by the difference between the initial and final concentrations of aniline in the liquid phase. All experiments were run in triplicate and controls containing aniline only, were used to ensure accuracy.

2.5. Catalytic oxidation evaluation

All Beta zeolite samples with adsorbed aniline from the adsorption studies were tested in a catalyst testing rig as illustrated in Fig. 2. The rig consisted of a gas delivery system, a reactor and detector. The aniline loaded Beta zeolites (100 mg) were individually placed in the quartz reactor and held in place by quartz wool plugs. Before testing, the zeolite samples were pre-treated for 60 min in a stream of a 3% (v/v) oxygen–helium mixture at a flow rate of 50 cm³ min⁻¹. Each sample was then subjected to a temperature increase of 10 °C min⁻¹ up to 750 °C. Products leaving the reactor in the exhaust gases were continuously monitored using the

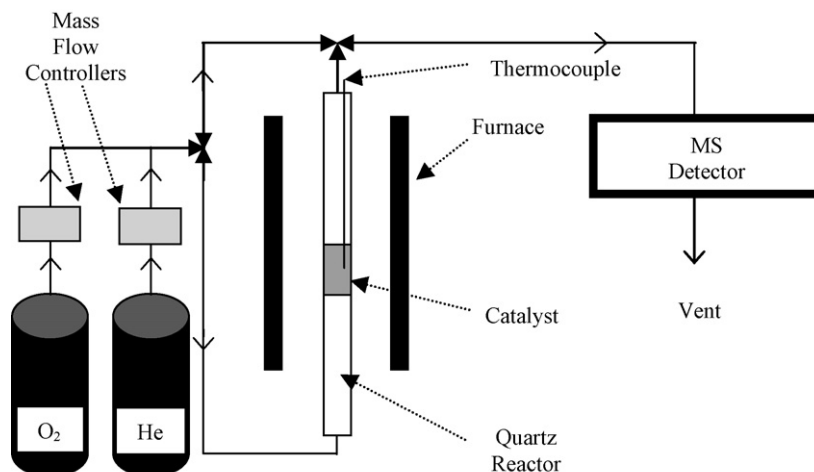


Fig. 2. Schematic of the catalytic oxidation setup.

mass selective detector (MSD). The MS results were collected by specialised Chemstation software HP5970C (Microsoft Windows based) on a Hewlett Packard 486S/20 personal computer.

2.6. Regeneration and re-use

For the regeneration and re-use studies the same mass of each Beta zeolite was successively put through a number of aniline adsorption and catalytic oxidation studies. The methodology for each cycle was in line with that outlined above for the adsorption and catalytic oxidation studies.

3. Results and discussion

3.1. Characterisation

The copper loading on each of the zeolites was 0.5% (w/w) and 1.4% (w/w) which corresponded to an ion-exchange level of 38% and 103%, respectively. 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. At exchange levels close to and above 100%, other copper species can also exist. These include Cu^{2+} ions at non-exchangeable sites (known as silica vacancy defects) and small clusters of copper particles [35,36]. This can account for the 'over-exchanged' catalysts. In this work zeolites with copper contents above 1.4% (w/w) were not tested as a loading of 1.4% (w/w) corresponded to 100% exchange and copper loadings above this level would promote the formation of large copper oxide particles which may be unstable under the adsorption conditions.

The surface areas of each of the copper-exchanged Beta zeolite adsorbents were estimated to be $579 \text{ m}^2 \text{ g}^{-1}$ for the 0.5% (w/w) loading and $548 \text{ m}^2 \text{ g}^{-1}$ for the 1.4% (w/w) loading as compared to $565 \text{ m}^2 \text{ g}^{-1}$ for the unmodified H-Beta ($\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 75:1). The X-ray diffraction pattern of the copper-exchanged zeolites showed no difference from that of the respective parent zeolite indicating good dispersion of the copper on the catalysts and the absence of any crystalline copper phase.

3.2. Stability of the copper loaded Beta zeolite

Leaching tests were undertaken on both the 0.5% (w/w) and 1.4% (w/w) Cu-Beta samples in order to assess the extent of copper leaching as a function of aqueous pH. The results of these studies are summarised in Table 1. From these results it is clear that both of the copper loaded Beta zeolites show optimum aqueous stability over the pH range 5–11. In this optimum pH range, the resulting aqueous leached copper concentrations were less than 1 mg dm^{-3} and at these levels the copper concentration in solution lies close to but within the typical industrial emission limit values (ELV's) for copper of 0.5 to 2.0 mg dm^{-3} [37]. In the pH range between pH 1 and 5, significant copper leaching occurred from the prepared adsorbent/catalysts giving resultant maximum aqueous concentrations of 16.5 and 44.7 mg dm^{-3} for the 0.5 and 1.4% (w/w) Cu-Beta samples. At all acidic pH's copper leaching was rapid and in all cases maximum leaching occurred in less than 30 min. A study into successive copper leaching from both copper loaded zeolites showed that no subsequent leaching occurs after initial leaching. Therefore in the pH range 5–11, both the 0.5 and 1.4% (w/w) Cu-Beta show

Table 1
Leaching tests undertaken on 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta over pH range 1–11

	0.5% (w/w) Cu-Beta					
pH	1	3	5	7	9	11
Copper leached (%)	97	48	1.4	0.9	0.7	2.2
Copper concentration _(aq) (mg dm^{-3})	16.5	8.2	0.23	0.15	0.12	0.37
Time to maximum leaching (min)	<30	<30	<30	<30	<30	<30
	1.4% (w/w) Cu-Beta					
pH	1	3	5	7	9	11
Copper leached (%)	95	38	1.7	2.1	1.5	1.5
Copper concentration _(aq) (mg dm^{-3})	44.7	17.9	0.8	1.0	0.7	0.7
Time to maximum leaching (min)	<30	<30	<30	<30	<30	<30

Reaction conditions: 500 mg catalyst, 150 cm^3 distilled water, 18 °C, 2 h.

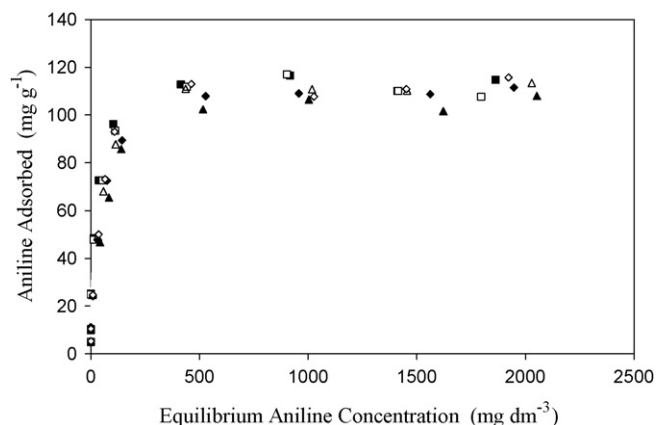


Fig. 3. Isotherms for aniline adsorption on H-Beta, 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta zeolites. (■) H-Beta at 6 °C; (□) H-Beta at 24 °C; (▲) 0.5% (w/w) Cu-Beta at 6 °C; (△) 0.5% (w/w) Cu-Beta at 24 °C; (◆) 1.4% (w/w) Cu-Beta at 6 °C; (◇) 1.4% (w/w) Cu-Beta at 24 °C.

optimal aqueous stability. The pH range during the aniline adsorption experiments ranged from pH 6.6 to 7.0 depending on the initial aniline concentration used. This adsorption pH range lies within the optimal pH range 5–11 which ensured minimal copper leaching.

3.3. Adsorption capacity of 0.5 and 1.4% (w/w) Cu-Beta for aniline

The results of the kinetic experiments undertaken on the H-Beta, 0.5 and 1.4% (w/w) Cu-Beta revealed that equilibrium aniline uptake for initial aniline concentrations of 125–1000 mg dm⁻³ occurred within approximately 5 min.

The adsorption isotherms for aniline uptake on the H-Beta, 0.5 and 1.4% (w/w) Cu-Beta were undertaken at 6 and 24 °C and are presented in Fig. 3. In all cases the shape of the adsorption curves are similar to that of a Type I profile as defined by the Brunauer classification whereby the isotherm approaches a limiting value [33]. All samples show maximum aniline adsorption of between 106 and 114 mg g⁻¹ suggesting that at this level each of the zeolites is saturated. There is only minimal difference in aniline uptake between the unmodified H-Beta zeolite and its copper modified forms and the levels of uptake are largely unaffected by temperature. The significant level of uptake indicates that the large pore diameters of the Beta zeolite facilitate removal of significant quantities of aniline from an aqueous environment.

The Langmuir model as defined below in Eq. (1) was applied to the adsorption data [38].

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

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 Eq. (1) was drawn to determine the values of K_L (intercept) and A_L/K_L (slope). Maximum uptake on the zeolite

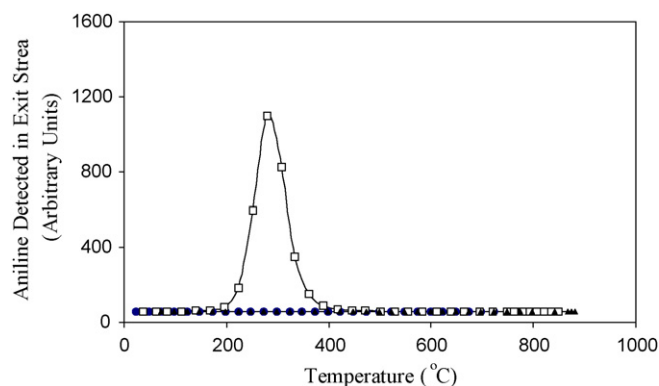


Fig. 4. Desorption of aniline from the Beta zeolites. (Conditions: 100 mg of zeolite sample containing 10.5 mg aniline, 3% (v/v) O₂/He gas flow, temperature ramped at 10 °C min⁻¹) (□, H-Beta; ▲, 0.5% (w/w) Cu-Beta; and ◆, 1.4% (w/w) Cu-Beta).

adsorbent surface was then obtained as K_L/A_L . The outcomes for the Langmuir isotherm plots are presented in Table 2 and clearly indicate that the sorption of the aniline from aqueous solution onto the H form and copper modified forms of Beta zeolite showed a very good fit to the Langmuir model approach.

Aniline is a weak base and at low pH's less than pH 5 forms the positively charged anilinium cation. The percentage of the unionised versus ionised forms of aniline vary as a function of pH. At the pH range used in the adsorption experiments (pH 6.6–7.0), aniline should exist exclusively in the unionised form. In the unionised form it is probable that the delocalised π electron cloud of the aniline interacts with the protonated aluminium sites on the Beta zeolite material [26]. This delocalised π electron cloud of the aniline shows a weaker affinity for the copper bound aluminium sites on the zeolite as evidenced by the lower adsorption constants (K_L) associated with the 0.5% (w/w) Cu-Beta and the 1.4% (w/w) Cu-Beta adsorption results (Table 2).

3.4. Catalytic oxidation of adsorbed aniline

Given that in the first part of the process significant uptake levels of aniline are possible on the unmodified and copper modified Beta zeolites, the second stage in the process seeks to evaluate the feasibility of catalytically oxidizing the adsorbed aniline to carbon dioxide, water and nitrogen. The efficacy of the oxidation process was assessed by monitoring the composition of the outgas from the reactor. Fig. 4 illustrates the desorption profile for aniline over H-Beta, 0.5 and 1.4% (w/w) Cu-Beta during catalytic oxidation. The H-Beta sample was used as a comparator to assess the influence of copper loading on aniline oxidation. In the absence of copper on the H-Beta zeolite, unreacted aniline is clearly visible in the exhaust gases from the reactor, indicating limited catalytic oxidation with significant amounts of aniline simply desorbing and outgassing at high temperatures. The presence of copper on the zeolite, whether the 0.5 or 1.4% (w/w) loading, considerably reduces the concentra-

Table 2

Langmuir constants for aniline adsorption on H-Beta, 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta zeolite at 6 and 24 °C

Sample	Langmuir constants				R ²
	Temperature (°C)	K _L (dm ³ g ⁻¹)	A _L (dm ³ mg ⁻¹)	K _L /A _L (mg g ⁻¹)	
H-Beta	6	13.3	0.117	113.64	0.999
	24	27.0	0.245	109.89	0.998
0.5% (w/w) Cu-Beta	6	3.74	0.035	107.52	0.998
	24	4.84	0.043	113.64	0.999
1.4% (w/w) Cu-Beta	6	2.47	0.023	107.53	0.995
	24	2.96	0.028	106.38	0.996

Table 3

Percentage of aniline oxidized using H-Beta, 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta

Sample	Aniline oxidized (%)
H-Beta	43
0.5% (w/w) Cu-Beta	100
1.4% (w/w) Cu-Beta	100

tion of aniline in the exhaust gases indicating strong oxidation of the adsorbed aniline to breakdown products. The overall extent of aniline degradation is presented in Table 3.

The degradation of aniline sorbed on both 0.5 and 1.4% (w/w) Cu-Beta is accompanied by a corresponding increase in carbon dioxide level detected in the exhaust gases from the reactor as evidenced in Fig. 5. Conversion into carbon dioxide does not occur until temperatures higher than approximately 450 °C. Significantly, the carbon dioxide profiles in Fig. 5 also show that the presence of copper loading on the Beta zeolite effectively lowers the temperature required for oxidation of the aniline as evidenced by the lower temperature emission of the carbon dioxide. The higher copper loading (1.4% (w/w)) also seems to produce an increase in the extent of evolution of carbon dioxide as evidenced by the larger peak. Analysis of the areas under each curve (Fig. 5) revealed a relative carbon dioxide ratio in the outgas streams of 100:81:32 for the 1.4% (w/w) Cu-Beta, 0.5% (w/w) Cu-Beta and H-Beta, respectively. In a semi-quantitative way this may indicate a higher degree of carbon formation within the pores as the copper (catalytic) content of the zeolite is reduced. The presence of either of the two copper loadings on the Beta zeolite also produces a downward shift in the temperature required for carbon dioxide formation.

3.5. Products of aniline oxidation

In the case of the exhaust gas stream for the catalytic oxidation of aniline on the 1.4% (w/w) Cu-Beta, an assessment was made in respect of other breakdown products from the reactor. These compounds included water, nitrogen, nitrogen oxide, nitrogen dioxide and benzene. Table 4 outlines the peak area counts associated with each of these compounds in the outgas from the reactor. Clearly from this table the principal components of the outgas post oxidation include carbon dioxide, nitrogen and water with relatively minor amounts of benzene, nitrogen oxide and nitrogen dioxide being produced. The presence of trace amounts of benzene indicates that the breakdown process may proceed by the decomposition of the nitrogen group on the adsorbed aniline forming benzene. The benzene is then further oxidized in the presence of the

Table 4

Compounds detected in outgas from the reactor (1.4% (w/w) Cu-Beta, 100 mg sample, 3% (v/v) O₂ in He, 50 cm³ min⁻¹, 10 °C min⁻¹)

Exit stream component	Peak count	Temperature of peak (°C)
C ₆ H ₅ NH ₂	0	–
CO ₂	14,200	620
H ₂ O	1130	Variable
N ₂	3940	590
NO ₂	60	645
NO	50	590
C ₆ H ₆	60	400

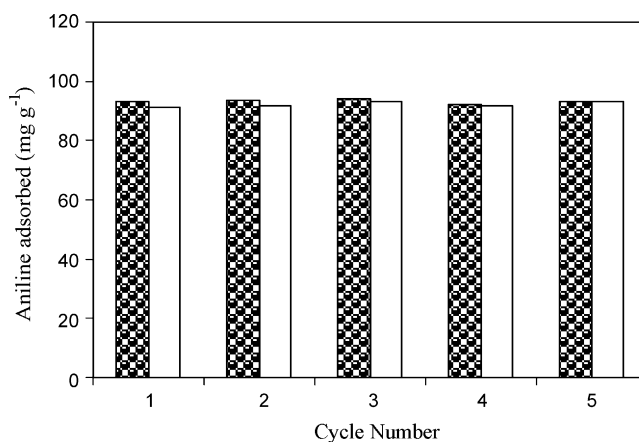


Fig. 6. Aniline adsorption on 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta during 5 successive cycles. (Conditions: 24 °C, 100 mg adsorbent, 10 cm³ of 1000 mg dm⁻³ aniline solution) (□, 0.5% (w/w) Cu-Beta; and ●, 1.4% (w/w) Cu-Beta).

catalyst to carbon dioxide and water. The formation of large quantities of nitrogen (compared to the oxides of nitrogen) would suggest that the nitrogen species from aniline are directly converted to N₂ or that any oxidized nitrogen species formed are reduced back to the N₂ in the presence of the hydrocarbons. Hydrocarbons are well known reducing agents for oxides of nitrogen forming N₂, water and carbon dioxide [39].

3.6. Regeneration and re-use of the copper loaded Beta zeolites

In practice three specific issues are essential to the continued regeneration and usage of this proposed two-stage system of adsorption followed by catalytic oxidation. In successive cycles, minimal copper leaching to the aqueous environment should take place, the aniline adsorption capacity must be maintained and the efficacy of the catalytic oxidation process for aniline degradation must not diminish significantly. Fig. 6 outlines the extent of aniline adsorption on the 0.5 and 1.4% (w/w) Cu-Beta during five successive cycles of the complete two-stage process (aniline adsorption followed by its catalytic oxidation). In the case of either copper loading on the zeolite, no reduction of aniline adsorption was observed from cycle 1 to cycle 5 indicating that the first step of the process, the adsorption step, is largely unaffected by the subsequent catalytic oxidation process. The results outlined in Table 5 indicate

Table 5

Percentage aniline oxidized as a function of the number of adsorption/oxidation cycles

Sample	Aniline in outgas (%)	Number of adsorption/oxidation cycles
0.5% (w/w) Cu-Beta	1	1
0.5% (w/w) Cu-Beta	14	5
1.4% (w/w) Cu-Beta	0	1
1.4% (w/w) Cu-Beta	6	5

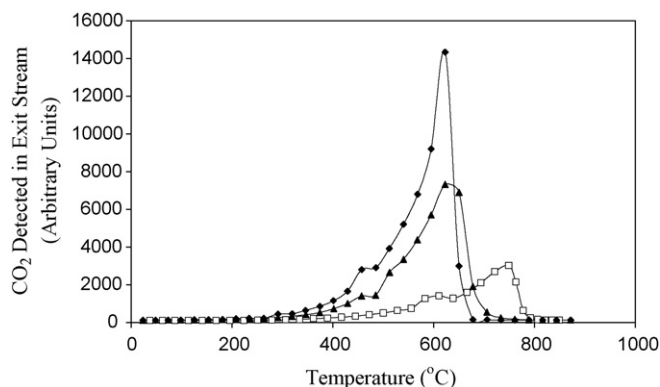


Fig. 5. Formation and desorption of CO₂ from the Beta zeolites. (Conditions: 100 mg of zeolite sample containing 10.5 mg aniline, 3% (v/v) O₂/He gas flow, temperature ramped at 10 °C min⁻¹) (□, H-Beta; ▲, 0.5% (w/w) Cu-Beta; and ◆, 1.4% (w/w) Cu-Beta).

that, in the case of the 0.5% (w/w) Cu-Beta, after the first cycle, 1% of the adsorbed aniline is detected in the outgas from the reactor. After five cycles, the aniline level detected in the outgas rises to 14%. This suggests some degree of catalytic oxidation capacity loss during successive cycles. In the case of 1.4% (w/w) Cu-Beta, no aniline is detected in the reactor outgas following the first cycle but 6% aniline is detected in the reactor outgas after five cycles, again suggesting some loss of oxidation capacity. The fact that the aniline adsorption uptake levels are undiminished after five cycles is not unexpected as the results outlined in Table 2 suggest that aniline uptake is largely independent of the presence or absence of copper on the Beta zeolite. In respect of possibility of copper leaching following regeneration, tests were carried out showing that 1.25% and 2.25% of the copper was leached from 0.5% (w/w) Cu-Beta and 1.4% (w/w) Cu-Beta, respectively following the first regeneration of the catalyst but from the second regeneration cycle onwards no further copper leaching from either catalyst occurred. The fact that the level of copper remains relatively constant over successive adsorption/catalytic oxidation cycles suggests that the losses in catalytic activity over these cycles is probably more related to the changing nature of than the loss of the copper on the zeolite material. In this regard, it is well known that exchanged copper, in particular when exchanged with ZSM-5 zeolites, can be transformed into CuO or Cu₂O particles when subjected to high temperatures (above 500 °C) in the presence of water vapour [40]. This overall effect leads to catalyst deactivation. Although conditions are not as harsh in the system presented in this work it is likely that copper movement, driven by the high temperatures required for regeneration, would result in some formation of these copper oxide species. The growth of these species primarily occur within the internal pore systems of the zeolites and therefore are not leached during the adsorption process. The presence of copper oxide particles was checked using XRD but the formation of copper oxide particles was not detected. However, it is likely that the size of these particles is so small that they will not be detected by XRD. There is also the added possibility that the oxidation process did not completely remove all of the adsorbed species and this could lead to some blocking of active sites responsible for the destruction of the adsorbed organic.

4. Conclusions

The basis of this research has been to develop a material which can function as both an adsorbent and as a catalyst in the adsorption and catalytic oxidation of a selected organic compound from an aqueous solution. The adsorbent/catalyst material chosen was a copper modified Beta zeolite and aniline was used as the selected organic compound. 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.

Removal of the aniline from aqueous solution has been shown to be effective with aniline uptake levels of 114 mg g⁻¹ being achieved with the 1.4% (w/w) Cu-Beta zeolite. This removal process allows for the potential recycling of the treated aqueous solution. Incorporation of this copper loading subsequently resulted in both complete oxidation of the adsorbed aniline and a reduction in the temperature necessary for the oxidation process. The products predominantly formed during the oxidation process were carbon dioxide, water and nitrogen, with minimal formation of benzene, nitrogen oxide and nitrogen dioxide.

Regeneration of the adsorbent/catalyst in this dual adsorption and catalytic oxidation system was also shown to be a feasible process. Successive adsorption/catalytic oxidation cycles showed that the 1.4% (w/w) Cu-Beta was the most effective material. The ani-

line adsorption levels on this material remained unchanged over five cycles. The leaching of copper during this aqueous adsorption stage for each of these cycles remained low and resulted in aqueous concentrations of less than 1 mg dm⁻³. The efficacy of the catalytic oxidation process in the breakdown of aniline remained strong over the five cycles but small concentrations of unreacted aniline were observed in the reactor outgas by the end of the fifth cycle. Whilst the system has shown considerable promise to this point, further work is currently being carried out specifically to address a number of key issues including the mechanism by which the catalytic oxidation process occurs, potential selectivity towards specific organics, de-activation of the 1.4% (w/w) Cu-Beta adsorbent/catalyst and the physical development of a larger scale system.

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