



# Zeolite ‘adsorption’ capacities in aqueous acidic media; The role of acid choice and quantification method on ciprofloxacin removal



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## ABSTRACT

Zeolites prepared from coal fly ash were used for the ‘adsorptive’ removal of the antibiotic, ciprofloxacin from aqueous solutions. Synthesised zeolites and other standard zeolites were characterised using XRD, FTIR and SEM analysis, to determine their formation, crystalline phase, morphology and elemental composition. The effect of acid type used for pH adjustment on the adsorption behaviour of ciprofloxacin on zeolites was investigated. Residual ciprofloxacin solutions after contact with zeolites were comparatively monitored using UV-Vis spectrometric and LC-MS TOF/DAD chromatographic methods. Results obtained, indicated formation of pure phase low silica zeolites. Removal efficiency by the synthesised zeolites for ciprofloxacin was significantly higher in acetic acid (92–94%) compared to HCl (27–61%) at pH 3 emphasising a clear dependence of results on experimental conditions. At experimental pH, the zeolites underwent chemical changes that were linked to structural changes. The presence of organic substrate during the chemical changes may probably explain side reactions, which led to by-products of organic origin reported in this contribution. FTIR and SEM images are presented after adsorption and clearly showed changes in zeolite structures. A discuss on the use of conventional UV-Vis spectroscopic, and LC-MS-TOF/DAD chromatographic method for quantification of aqueous residual ciprofloxacin after the ‘adsorption’ process is also presented and highlights the shortcomings of the former method compared to the latter. The zeolites showed promise for aqueous ciprofloxacin remediation reducing chemical oxygen demand (COD) levels, with process mechanisms supporting chemical interactions with substrate in a manner similar to degradation reactions.

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## 1. Introduction

Approximately 90% of electricity in South Africa is derived from coal combustion, and about 5–20% of the coal mass remains as fly ash and bottom ash after combustion [1]. Worldwide, an estimated 500 million tonnes (Mt) of fly ash is produced from coal combustion annually. However, only about 20–30% of the generated coal fly ash is utilized for sludge stabilization, reclamation, decontamination of less fertile soil agriculture [2], while the bulk of the generated coal fly ash is disposed off as landfill and classified as a human carcinogen [3]. Due to shortage of landfill sites, a number of

studies have considered zeolitization as one of the novel method to recycle fly ash [4–6]. Converting fly ash into zeolites not only alleviates the disposal problem but turns waste material into a value added product. This material has also been utilized in various industrial applications ranging from use as molecular sieves [7,8], heterogeneous catalyst [9–11], catalyst supports [9,12,13] and many others.

Zeolites are microporous crystalline aluminosilicates, composed of TO<sub>4</sub> tetrahedra (T = Si or Al) with oxygen atoms connecting neighbouring tetrahedra. Their unique properties is attributed to their aluminosilicate surfaces which serve as active sites for chemical reactions, and a cage structure used as clathrate for molecular entrapment. The latter property has advanced research on the use of zeolites as adsorbents for various organics and metals [11,12,14,15].

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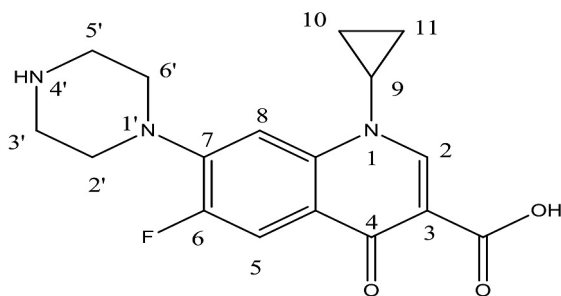
Model organics currently reported in adsorption studies range from simple phenols such as phenol, p-chlorophenol, biphenol A [11–13] to pharmacologically active compound (PhCd) such as ciprofloxacin, enrofloxacin, erythromycin, carbamazepine and levofloxacin [15–18]. Several reports have indicated that these compounds are readily adsorbed on zeolites surfaces and/or held within the interstices of the highly porous material. Findings from previous studies showed that typical removal efficiencies of zeolites have ranged from 48.9 to 53% for ciprofloxacin [17,19,20], and from 50 to 85% for phenol [21,22].

In the pursuit of other possible applications of zeolites, this study investigated the use of zeolites as suitable adsorbents for removal of ciprofloxacin, a pharmaceutical contaminant in aqueous solution. Three types of zeolites were prepared from fly ash and characterised to compare with purchased standard zeolites of the same composition. As opposed to the conventional UV–vis spectroscopic technique widely reported in several researches for quantification of aqueous organics, we monitored residual aqueous organic solutions using LC-MS-TOF. Our findings, here reported in an exploratory manner firstly highlights the influence of the acid used for pH control on the behaviour of zeolites and indeed the ‘adsorption’ results, and secondly identifies the conventionally reported spectroscopic method for measuring aqueous organic as particularly unsuitable in certain cases. By careful study of pristine and recovered zeolites, this contribution provides insightful experimental data and novel interpretations on the working operations of zeolites in acidic media. Ciprofloxacin (Fig. 1) has been utilized as model drug for many researches due to its persistence in the environment. It was selected as model organic in this study due to existing literature on the drug. It is globally used for the treatment of several bacterial infections in humans and animals. It can be excreted into water sources due to incomplete metabolism in humans or coming from the effluents of drug manufactures. It has been detected in water and wastewater at concentration typically < 1 µg/L [23,24], while in hospital effluents a range of 3–87 µg/L [25] and drug production facilities (31 mg/L) [24,25] was reported.

## 2. Materials and methodology

### 2.1. Materials

Coal fly ash used in this study was collected from the Matla power station situated in Mpumalanga, South Africa. Acetic acid (98%), acetonitrile (98%), ciprofloxacin standard (98%), formic acid (98%), sodium aluminate powder and sulphuric acid (97%) were purchased from Sigma-Aldrich, South Africa. Sodium hydroxide pellet (98%) was purchased from Merck chemicals. Ferrous ammonium sulphate, hydrochloric acid (32.00%), potassium dichromate, silver sulphate and mercuric sulphate were purchased



**Fig. 1.** Ciprofloxacin with fluorine atom at position 6, piperazine moiety at position 7, a cyclopropyl ring at position 1, carboxyl group at position 3 and quinolone ring at the central unit. Two existing pKa values, pKa,CO<sub>2</sub>H = 5.9 and pKa,N4' = 8.9.

from KIMIX chemicals. Zeolite standards were purchased from Zeolyst international. GHP acrodisc syringe 0.22 µm filters were purchased from Separations, South Africa.

### 2.2. Preparation of zeolite from coal fly ash

Coal fly ash (CFA) was pre-treated by calcining at 800 °C (Scientific series 930 furnace, South Africa) for 2 h, followed by acid treatment with 0.3 M HCl to increase its activity in zeolite formation. The acid treatment de-aluminates the coal fly ash and reduces iron content, thereby increasing the activity, thermal stability and acidity of the zeolite. The calcined treated coal fly ash (CTCF) was used for preparation of zeolite materials.

#### 2.2.1. Preparation of zeolite A

Zeolite A was prepared according to reported literature method [6]. CTCFA and NaOH (pellets) were combined in the ratio of 1.25:0.8 (w/w), and ground to form a homogeneous mixture. The mixture was fused at 650 °C for 1 h, cooled, comminuted and mixed in 300 mL of millQ water. The mixture was transferred into a 1 L polypropylene bottle, sealed and stirred in an oil bath at 100 °C for 2 h, cooled and filtered. Exactly 100 mL of aluminium solution (previously prepared by mixing 2:3 ratio (w/v) of sodium aluminate powder with millQ water) was added to the filtrate in order to adjust the SiO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O/SiO<sub>2</sub> and H<sub>2</sub>O/Na<sub>2</sub>O ratio in the solution. The solution was stirred for 30 min at room temperature, raised to 90 °C and held for 1.5 h, and further raised to 95 °C and held for 2.5 h. The precipitated zeolite was centrifuged, washed with millQ water until the pH of the solution was neutral. The precipitate was dried at 100 °C (Scientific series 900 oven, South Africa) for 2 h. The powder zeolite A obtained was stored in a vial for further use.

#### 2.2.2. Preparation of zeolite Y

Zeolite Y was prepared according to reported literature method [5]. CTCFA and NaOH in the ratio of 0.8:1.5(w/w) were ground and mixed to form a homogeneous mixture. The mixture was fused at 550 °C for 2 h. The fused mixture was cooled, comminuted and mixed in 500 mL millQ water. The resulting slurry was aged for 10 h while stirring. The aged (sodium aluminate) slurry formed was subjected to hydrothermal crystallization at 100 °C for 17 h. Crystallized zeolite was cooled and filtered using a Whatman 1 filter paper, washed with MillQ water to remove excess aluminium and oven dried at 50 °C. The powdered zeolite Y was stored in a vial for further use.

#### 2.2.3. Preparation of zeolite X

Zeolite X was prepared according to reported literature method [4]. In brief, about 1:2 ratios of NaOH and (CTCFA), was milled and fused at 650 °C for 1 h. The resulting fused mixture was cooled at room temperature, comminuted and mixed in 100 mL millQ water. The slurry obtained was stirred in a glass beaker for 24 after which the mixture was kept at 90 °C for 6 h without any disturbance. The precipitated zeolite was repeatedly washed with millQ water to remove excess sodium hydroxide, filtered using a Whatman 1 filter paper and dried at 80 °C for 24 h. Sodium hydroxide added to the fly ash serves as an activator, and also adjusts the sodium content in the starting material.

### 2.3. Characterization of zeolites and CFA

The morphology, and surface texture of individual particles and the elemental composition of the zeolite samples were analysed by means of high resolution scanning electron microscopy (HR-SEM) (Auriga instruments, USA), equipped with secondary electron

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