



## ADSORBENT FROM WASTE AND NATURAL DEPOSITS FOR PARAQUAT REMOVAL IN WATER

(Penjerap daripada Sisa Industri dan Semulajadi untuk Penyingkiran Paraquat di dalam Air)

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### Abstract

Studies on the removal of frequently used herbicide for controlling broad-leafed weeds, Paraquat Dichloride (PQ) has been carried out intensively. Waste from steelmaking industries (Electric Arc Furnace (EAF) slag) and natural zeolite (clinoptilolite) were used as the starting materials. Preparation of an adsorbent involved two steps, namely extraction iron oxide (IO) from slag and precipitation of IO onto clinoptilolite. Characterization of NZIC were done using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), single-point Brunauer Emmett Teller (BET) surface area analysis, Vibrating Sample Magnetometer (VSM) and pH at zero point charge (pHzpc). The NZIC showed a lower magnetic saturation at 8.13 emu/g compared to maghemite at 29.5 emu/g. The BET surface area of NZIC was 146.29 m<sup>2</sup>/g, larger compared to the individual surface area of clinoptilolite and maghemite which are 37.84 and 17.84 m<sup>2</sup>/g respectively. Adsorption of PQ onto clinoptilolite and NZIC were investigated using a batch experiment. Surface characteristic of NZIC was investigated by pHzpc experiment showing that at pH 8.2 its electric surface charge is zero. Optimum parameters for adsorption of PQ in water were found at pH 12 with 0.01 g/10 mL of NZIC and equilibrium time of 20 minutes. Desorption experiment revealed that NZIC have a good recovery in repetitive usage for PQ removal in water.

**Keywords:** waste, clinoptilolite, iron oxide, paraquat, adsorption

### Abstrak

Kajian ke atas penghapusan racun rumpai yang sering digunakan untuk mengawal tumbuhan berdaun besar, Paraquat Diklorit (PQ) telah dijalankan secara intensif. Sisa daripada industri keluli dan zeolit asli (klinoptilolit) telah digunakan sebagai bahan mentah. Elektrik relau arka (EAF) sanga mengandungi logam oksida berharga seperti oksida besi (IO) yang merangkumi 37% (w/w) sanga. Kajian ini memberi tumpuan untuk mengekstrak IO dan pemendakan ke atas klinoptilolit. Penyediaan Zeolit-Besi Oksida Komposit (NZIC) melibatkan dua langkah mudah iaitu pengekstrakan IO dari sanga EAF dan pemendakan IO ke atas klinoptilolit. Pencirian NZIC telah dilakukan dengan menggunakan Fourier Transform Inframerah Spektroskopi (FTIR), Imbasan Elektron Mikroskopi (SEM), analisis kawasan permukaan Brunauer Emmett Teller (BET), Vibrating Sample Magnetometer (VSM) dan pH di caj titik sifar (pHzpc). NZIC menunjukkan ketepuan magnet yang rendah iaitu pada 8.13 emu/g berbanding maghemite dengan ketepuan magnet 29.5 emu/g. Kawasan permukaan BET untuk NZIC adalah 146.29 m<sup>2</sup>/g, lebih besar berbanding dengan kawasan permukaan individu klinoptilolit dan maghemite, 37.84 dan 17.84 m<sup>2</sup>/g masing-masing. Penjerapan PQ ke atas klinoptilolit dan NZIC telah disiasat menggunakan eksperimen kumpulan. pHzpc untuk NZIC adalah pada pH 8.2 di mana caj permukaannya adalah seimbang. Parameter optimum untuk penjerapan PQ dalam air didapati pada pH 12 dengan 0.01 g/10 mL NZIC dan keseimbangan masa iaitu 20 minit. Eksperimen penyaherapan menunjukkan NZIC mempunyai kadar pemulihan yang baik dalam penggunaan berulang-dalam penyingkiran PQ di dalam air.

**Kata kunci:** sisa, clinoptilolit, ferum oksida, paraquat, penyerapan

### Introduction

Paraquat (1,1'-dimethyl-4,4'-bipyridinium) is a highly effective herbicide used to control weeds and grass in agricultural area. Commonly, farmers tend to spray the diluted herbicides to the plant area and eventually the excess PQ may reach the source of fresh water by leaching from soil. Paraquat (PQ) is hydrophilic compound and it is highly soluble in water. Paraquat is classified as toxic to human and environment. The maximum concentration level (MCL) of PQ in drinking water is 20 µg/L according to United States Environmental Protection Agency (USEPA). Hence, efficient method for pesticides removal in water is constantly being researched. Various techniques has been research including adsorption [1, 2] and advanced oxidation process (AOP) via catalyst and Fenton [3-5]. Adsorption is considered a feasible method for pesticides removal due to its simplicity, cost-effectiveness and high removal.

The use of agricultural and industrial waste as precursors in the preparation of adsorbent constantly studied. In this study, electric arc furnace (EAF) slag and clinoptilolite were used as the starting materials for the production of an adsorbent. Natural zeolite namely clinoptilolite is a cation exchanger and have high selectivity properties. The selectivity and size exclusion of zeolite offers more effective removal of PQ. The performance of synthetic and natural zeolite in removing contaminants is not much different [6]. Zeolites also reduce the effect of NOM in adsorption of contaminant in real water sample [7].

The EAF slag is a highly available material from steel-making industry wastes and comprised of many valuable metal oxides such as Zinc (Zn), Iron (Fe), Calcium (Ca), Copper (Cu) and Manganese (Mn) [8]. Numerous works have been reported on the recovery of these valuable materials from slag. For example, Saufi [8] extracted Fe to use to enhance its carbon nanotube (CNT). On the other hand, Shawabkeh [9], Fallman [10] and Orhan [11] studied on maximizing Zinc, Chromium and Barium recovery from slag. In this work, iron oxide was extracted from EAF slag and precipitated onto clinoptilolite to produce an adsorbent for the removal of PQ in water.

### Materials and Methods

#### Raw material

Electric arc furnace slag was collected from Antara Steel Mills (M) Sdn.Bhd and clinoptilolite was purchased from Shafzan Feed and Fertilizer. Both raw materials were ground and sieved to a particle size of 75 µm prior to use. Clinoptilolite was first activated by agitating in 2M sodium chloride (NaCl) solution [12]. Paraquat standard was purchased from Fluka Analytical and used without further purification. Stock solution of PQ was prepared by dissolving standard paraquat in double distilled water. The working solution of PQ was prepared by series of dilution from the stock solution prepared.

#### Preparation of Natural Zeolite-Iron Oxide Composite (NZIC)

The NZIC was prepared via two simple steps. First, iron oxide (IO) was extracted from EAF slag, followed by the precipitation of iron (hydr)oxide onto clinoptilolite. Powdered EAF slag was added to ammonium chloride (NH<sub>4</sub>Cl) solution and the mixtures were refluxed for 2 hours. A desired amount of clinoptilolite was added to the filtrate solution to make a 3 to 1 amount of clinoptilolite to iron oxide. Concentrated sodium hydroxide (NaOH) was added dropwise to the filtrate with an aid of sonication. The mixture was stirred for another 2 hours until homogenous suspension was obtained. Synthesized product was filtered, washed and dried overnight in an oven at 70°C. Final product was calcined in a box furnace at 500°C for two hours at a temperature rate of 10 °C/min.

#### Characterization of NZIC

Fourier Transform Infra-red (FTIR) spectroscopy (Perkin Elmer, Spectrum One) was used to analyse the functional groups found in the clinoptilolite and NZIC prepared at a spectral range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The morphology of clinoptilolite, maghemite and NZIC were observed using Scanning Electron Microscopy (SEM) (Phenom G2 Pro). Effect of surface area of clinoptilolite, maghemite and NZIC were studied using single-point Brunauer Emmett Teller (BET) surface area analysis. Magnetic properties of maghemite and NZIC were analysed using Vibrating

Sample Magnetometer (VSM) at room temperature. Zero point charge (zpc) of NZIC was determined by pH at zero point charge (zpc) experiment [13].

### Removal of Paraquat in water by NZIC

Adsorption experiment for study on were effect of time, adsorbent dosage and pH in paraquat removal by NZIC were conducted in a batch mode study. The experiment take place in thermostat orbital shaker (Lab Companion) and experiments were repeated to ensure the reproducibility of the result is obtained. Adsorption and desorption experiment were done using 10 mg/L PQ standard solution followed by desorption with distilled water. Initial and final concentration of PQ was quantified using calibration curve of PQ standard, analysed by UV-Vis spectrophotometry (UV-Vis-Perkin Elmer Lambda25 Spectrophotometer) at maximum absorption wavelength of 257 nm.

## Results and Discussion

### Characterization of NZIC

#### Fourier Transform Infra-red

Spectra of clinoptilolite, maghemite and NZIC in Figure 1 showed an intense peak at  $1028\text{ cm}^{-1}$  indicates the presence of internal vibration of tetrahedral Si-O and Al-O. At  $450\text{ cm}^{-1}$  band showed the vibration of O-Al-O or O-Si-O bonds. The existence of in-plane-bending vibration of water ( $\text{H}_2\text{O}$ ) and OH bending in clinoptilolite and maghemite observed at  $1637\text{ cm}^{-1}$  and  $3447\text{ cm}^{-1}$  respectively were due to moisture in the sample preparation. Low band at wavenumber of 600 and  $790\text{ cm}^{-1}$  found at spectrum of maghemite and NZIC were attributed to the characteristics band of iron oxide [14].

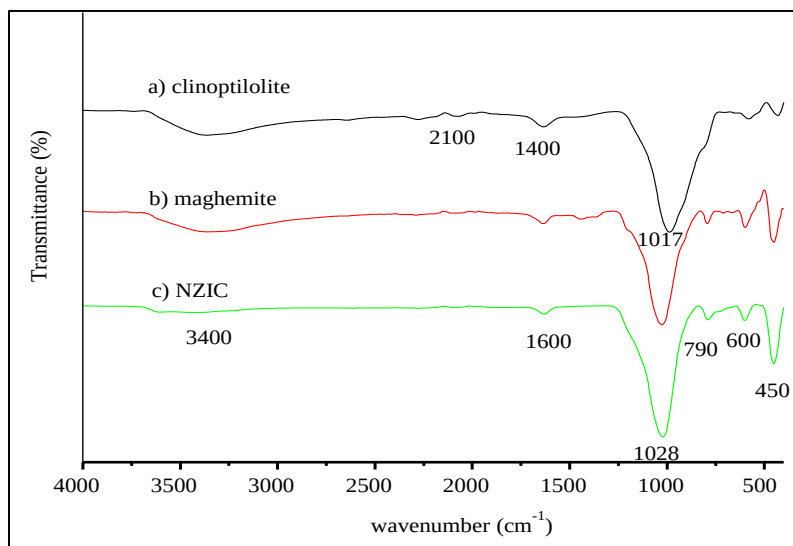


Figure 1. IR spectra of a) clinoptilolite, b) maghemite, and c) NZIC

#### Scanning Electron Microscopy micrograph

SEM images of clinoptilolite, maghemite and NZIC were shown in Figure 2. Micrograph in Figure 2a showed an irregularly shaped of clinoptilolite. Maghemite poses a prismatic and flake-like shape as observed in Figure 2b. Maghemite was scattered around clinoptilolite in Figure 2c showing the effective effect of dispersive by sonication in preparation of NZIC procedure.

### Magnetic saturation

Figure 3a showed the hysteresis loop for maghemite and NZIC analysed by VSM at room temperature indicate curve for paramagnetism materials. Magnetic saturation of maghemite and NZIC were 29.55 and 8.13 emu/g respectively. Magnetic curve of maghemite and NZIC showed small loop indicating the remaining of magnetic reflux in the sample eventhough magnetic force is zero. Figure 3b suggested that NZIC in water was attracted effectively when external magnetic field was introduced. The decreasing effect of magnetic saturation in NZIC sample was due to small amount of maghemite in per gram of NZIC.

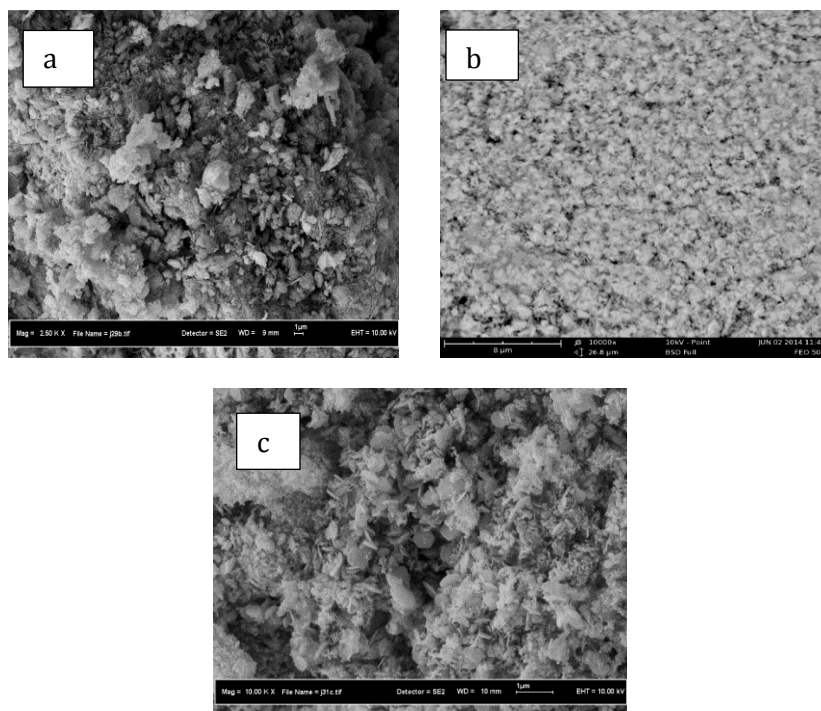
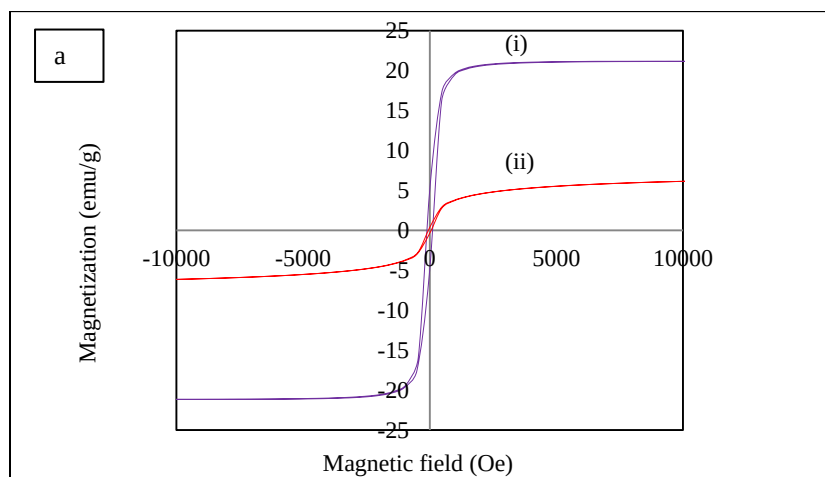


Figure 2. Micrograph of a) clinoptilolite, b) maghemite, and c) NZIC



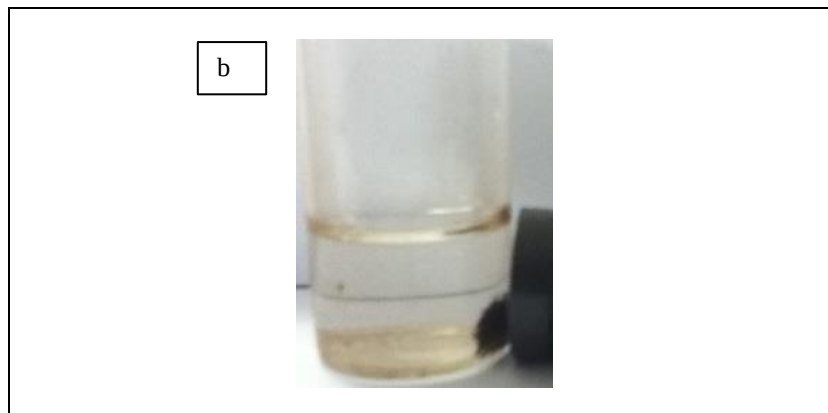


Figure 3. a) Magnetization curve of i) maghemite and ii) NZIC at 300 K, and b) magnetic attraction of NZIC towards external magnetic application

### Surface area

The surface areas of raw materials, clinoptilolite and EAF slag as well as maghemite and NZIC were presented in Table 1. Iron oxide showed a small surface area due to the agglomeration effects and its mutual magnetic attraction. By modification of maghemite with clinoptilolite, the surface area increase almost four fold. The larger surface area of an adsorbent, then the bigger active site available for adsorption to take place.

Table 1. Surface area of clinoptilolite, EAFS, iron oxide and NZIC

| Sample                          | Clinoptilolite | Raw EAFS | Maghemite | NZIC   |
|---------------------------------|----------------|----------|-----------|--------|
| Surface area, m <sup>2</sup> /g | 37.84          | 3.02     | 9.62      | 146.29 |

### pH at zero point charge

The pH at zero point charge (pH<sub>zpc</sub>) for NZIC was determined by mixing 0.15 g NZIC in 0.01 M concentration of NaCl and varying the pH of the solution from pH 2-13. After 24 hours agitation, the resulting mixtures were analysed for its pH. The plot of initial and final pH in Figure 4 showed an intersection of the two curves at pH 8.2. At this point, the NZIC charge is considered neutral. The adsorption of PQ depends on the pH of solution as PQ exists in its cationic form in water. At lower pH, surface of NZIC was saturated with hydronium ions (H<sub>3</sub>O<sup>+</sup>), thus high competition of these positively charge paraquat (PQ<sup>+</sup>) and H<sub>3</sub>O<sup>+</sup> decreased the adsorption of PQ.

### Paraquat removal by NZIC

Figure 5 shows the plots of PQ removal by clinoptilolite, maghemite and NZIC against time. Adsorption of PQ by clinoptilolite and NZIC (3:1) were rapid at first and reached plateau after 20 minutes contact time. The equilibrium time of PQ removal was attained at the 20th minutes. From the graph in Figure 5, maghemite showed a very low adsorption, means that maghemite was not a good adsorbent. Although the surface area of NZIC was higher than clinoptilolite, but, the removal of paraquat by clinoptilolite was slightly higher than NZIC. As observed in Figure 5, low removal of PQ observed. Hence, high surface area of NZIC resultant lower because of maghemite in NZIC was not functioning as an adsorbent.

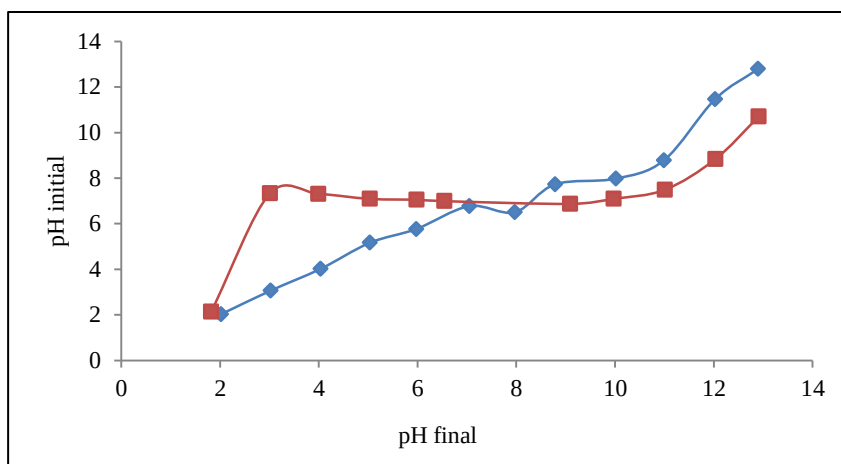


Figure 4. The pH at zero point charge of NZIC

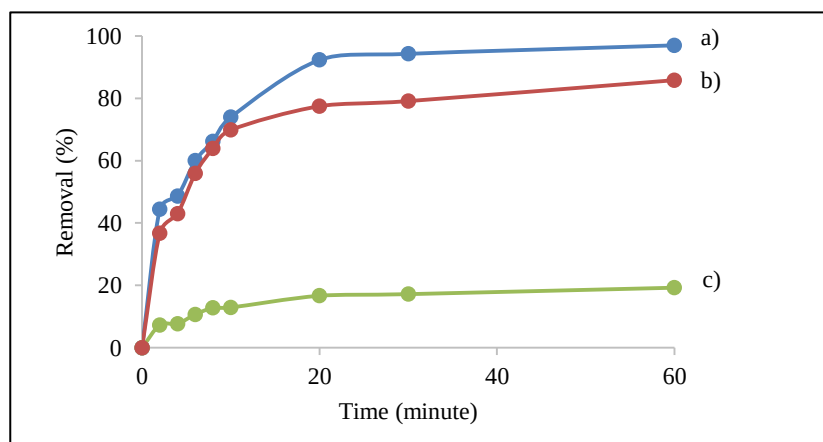


Figure 5. Comparison on the PQ removal by a) clinoptilolite, b) maghemite and c) NZIC (initial PQ concentration = 10 mg/L, Adsorbent dosage = 0.01 g, pH = neutral)

Plot in 6 indicate that paraquat uptake increased with increasing pH. Maximum PQ uptake was obtained at pH 12. The removal of PQ is highly dependent on initial solution pH. This condition interrelated with the nature of PQ in water. The  $pK_a$  value of cationic PQ is 9 – 9.5 [14]. At higher pH than  $pH_{zpc}$ , higher concentration of hydroxide ions ( $OH^-$ ) was present on NZIC surface. Hence, NZIC acquired a negatively surface charge at higher pH and cationic PQ easily attached to the surface of NZIC via attraction force.

Figure 7 shows revealed that NZIC have a good recovery of PQ in desorption experiment. At first adsorption-desorption experiment, 99 % of PQ was adsorbed and desorbed into the solution. The performance of PQ removal after second and third time repetitive usage was decreased to 86 %. This small decreasing in percentage removal of PQ showed that the stability of these adsorbent for repetitive usage.

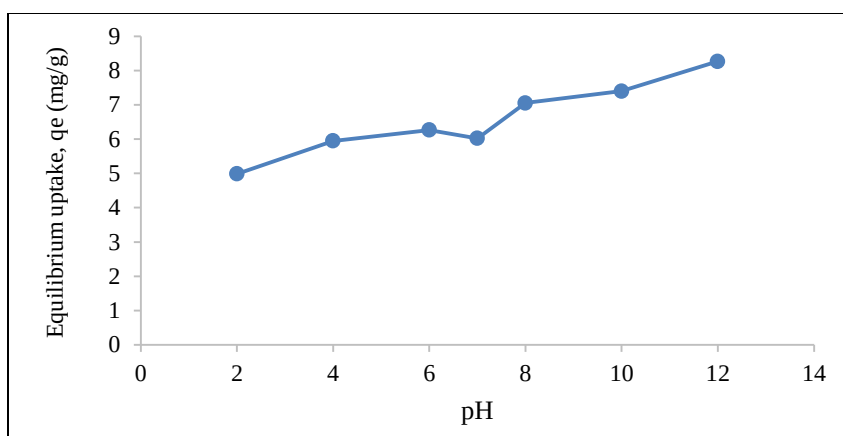


Figure 6. Effect of pH on PQ uptake by NZIC (initial PQ concentration = 10 mg/L, Adsorbent dosage = 0.01 g, pH=12)

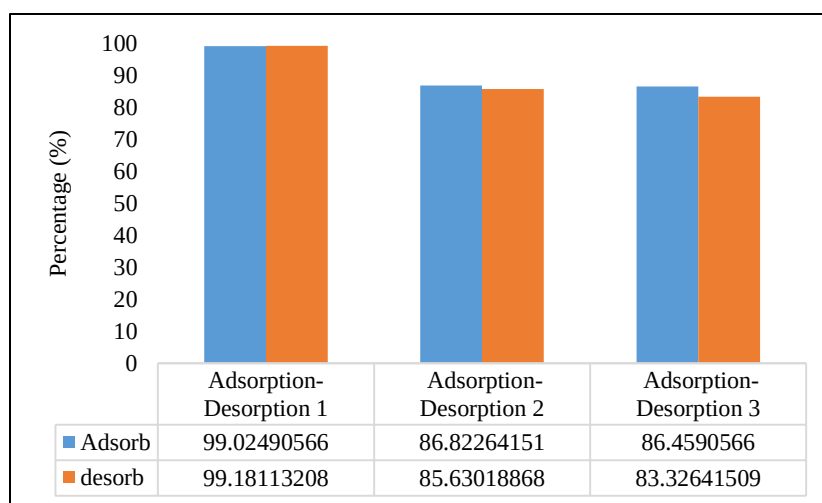


Figure 7. Repetitive adsorption of PQ onto NZIC (initial PQ concentration = 10 mg/L, Adsorbent dosage = 0.01 g, pH = 12)

### Conclusion

Preparation of NZIC was done by extraction of iron oxide (IO) from slag and precipitation of IO onto clinoptilolite. Magnetization analysis of NZIC revealed the ability of maghemite in NZIC as a magnetic separator when external magnetic field was applied. Preliminary study showed that clinoptilolite have higher removal percentage of paraquat (96%) compared to NZIC (86%) due to nature of maghemite which is not a good adsorbent. Optimum parameters for adsorption of 10 mg/L PQ in water were found at pH 12 with 0.01 g of NZIC with equilibrium time of 20 minutes. Desorption experiment demonstrate that NZIC as a stable adsorbent for repetitive usage for PQ adsorption.

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