



## A Comparative Study of Modified Lignite Fly Ash for the Adsorption of Nickel from Aqueous Solution by Column and Batch Mode Study

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### Abstract

The removal of  $Ni^{2+}$  from an aqueous solution using fly ash was modified by alkali (FAN), alkali and dye modified fly ash (FAN-MO) were compared. The influence of the four parameters (solution pH, contact time, initial metal ion concentration and dose of the adsorbent) on the removal of  $Ni^{2+}$  at  $27 \pm 5^\circ C$  was studied by batch mode and column study. The adsorption of  $Ni^{2+}$  was higher at pH 3 for FAN (95.45%) in batch mode study and 57.4% in column study. For FAN-MO at pH 5, the adsorption was 89.2% in batch mode study and 74.69% in column study. The maximum adsorption of  $Ni^{2+}$  onto FAN and FAN-MO was achieved at 50 minutes. The linear forms of Langmuir, Freundlich, Tempkin, D-R, Harkin-Jura and Frenkel Halsey isotherms were utilised for experiments with varying metal concentrations. The adsorption of  $Ni^{2+}$  ions satisfies only Langmuir isotherm model. Influence of  $Cu^{2+}$  ions and  $Zn^{2+}$  ions on adsorption of  $Ni^{2+}$  ions on FAN and FAN-MO in binary and tertiary systems showed certain decrease of adsorption ability.

**Keywords:** Alkali-activation, batch mode studies, column studies.

### Introduction

Coal/Lignite based Thermal Power Generation has been the backbone of capacity addition in the country. Indian coal is of low grade having high ash content up to 40% in comparison to imported coals which have ash content of the order of 10-15%. Large quantity of ash is being generated at coal/lignite based Thermal Power Stations in the country, which has been one of the sources of pollution of both air and water. The demand for industrial and domestic energy results in the production of a large volume of fly ash from solid coal fuel, which will increase in the world on an unprecedented scale during the next years. Therefore, fly ash should not only be disposed of safely to prevent environment pollution, but should be treated a valuable resource<sup>1</sup>. Traditionally, fly ash has been used as pozzolanic material to enhance physical, chemical and mechanical properties of cements and concretes. However, only amounts of 20-30% of fly ash have been currently used for this purpose while remaining 70-80% is land filled or surface-impounded. For the remaining material, disposal practices involve holding ponds lagoons, landfills and slag heaps, all of which can be regarded as unsightly, environmentally undesirable and / or a non-productive use of land resources, as well as posing an on-going financial burden through their long-term maintenance. Furthermore, for those coal power plants located in urban areas, finding disposal sites must be well managed, so that local surface and ground water supplies are protected. This can cause significant economic burden to achieve the necessary water and land management. These factors have prompted researchers to look for alternative usages for fly ash, other than the cement and construction industry<sup>2</sup>. Most of the fly ashes from the

combustion of coal are made up of aluminosilicate and silica glasses with small amounts of crystalline materials, including mullite, quartz, haematite, and magnetite<sup>3</sup>. The reactivity of a fly ash depends upon many parameters, most important of which are chemical and mineralogical composition of fly ash, curing temperature and the use of chemical activators<sup>4,9</sup>. The use of fly ash for the heavy metals removal, from wastewaters resulted in the dye finishing industry, faces a supplementary problem, related to the dyes affinity for oxide surfaces. Previous studies proved that further conditioning by alkali treatment can be needed for enhancing the adsorption efficiency of heavy metals<sup>10</sup>, or multi component systems of heavy metals and dyes, on fly ash. Good efficiencies of heavy metals removal were obtained on fly ash treated with 2N NaOH solutions<sup>11</sup>. Some dyes fixed on the fly ash surface can act as complexation agents, increasing the adsorption efficiency of the heavy metals.

Every development in science and technology brings in new problems. Now, it's for us to decide, how we intend to use the power of technology placed in our hands. The presence of heavy metals in the aquatic ecosystem has been of increasing concern because of their toxic properties and other adverse effects on natural waters quality, such as Ni, Cu, Zn, Cr, Cd and Pb find its way to water bodies through waste water from metal plating industries, cadmium – nickel batteries and alloys. Exposure to nickel causes decrease in body weight, heart and liver damage and skin irritation. Nickel powder (T; R48-23) has been classified in chronic toxicity classification as per environmental risk assessment report on nickel.  $NiSO_4$ ,  $NiCl_2$ ,  $NiCO_3$  and  $NiNO_3$  are classified as carcinogen class I (by inhalation), reproductive toxicants class II (may cause harm to unborn

children) and chronic toxicants (T; R48 23). If particle size of nickel powder found to be less than 0.1  $\mu\text{m}$ , it is classified as T; R52-53 (harmful to the aquatic environment)<sup>12,13</sup>. The higher concentration of Ni(II) in ingested water may cause severe damage to lungs, kidneys, gastrointestinal distress, e.g., nausea, vomiting, diarrhoeas, pulmonary fibrosis, renal oedema, and skin dermatitis. It is also a known carcinogen<sup>14</sup>. The average concentration in the effluent from the plating plants ranges between 10 and 80 mg/l. Due to toxicity of metals, the Ministry of Environment and Forests (MOEF), Government of India, has set Minimal National Standards (MINAS) of 2.0 mg/l for Ni(II) for safe discharge of the effluents containing these metal ions into surface water<sup>15-18</sup>.

The presence of heavy metal in wastewaters is due to the discharge of many industrial units. This paper presents a comparative study of the efficiency of the Ni(II) uptake onto modified fly ash by alkali treatment 4N NaOH (FAN) and by Methyl orange (FAN-MO). The adsorption kinetics were studied and the substrate capacities are discussed and correlated with the surface structure (SEM and EDX) by batch and column study.

## Material and Methods

**Preparation of adsorbents:** The fly ash used for this study was collected from the NLC Power Plant, Neyveli, Tamil Nadu, India. One part of the fly ash was treated with 4N NaOH and then kept in magnetic stir at 90°C for 1 h. After that the solution was allowed to settle for 24 hrs. and washed with distilled water again and again till the conductivity of the filtrate was below 300  $\mu\text{S}$ . It was then filtered and dried in hot air oven at the temperature of 105°C. The dried alkali treated fly ash (FAN) was then powdered, ground and used for further studies<sup>19</sup>. It was divided into two parts and one part was used as such and the other part of the FAN was further treated with Methyl orange dyes for 48 hours at room temperature followed by filtration and flush with distilled water, dried (FAN-MO) and used for adsorption of Ni(II) ions. The yield for FAN was found to be 95.3% and for FAN-MO it was found to be 96%.

**Preparation of Adsorbate:** Nickel sulphate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), Zinc sulphate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), were purchased from Spectrum reagents and chemicals Pvt. Ltd., Adayar, Aluva. Copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), NaOH, HCl,  $\text{HNO}_3$ , were obtained in S D fine – Chem. Limited, Mumbai and used without further purification. Stock solutions were prepared by dissolving 1g/L double distilled water was used through out the study.

**Characterization of adsorbent: Acidity and basicity of adsorbent (Boehm titration):** Acidity and basicity were estimated by mixing 0.2 g of adsorbent (FAN and FAN-MO separately) with 20 mL of 0.1 M NaOH, 20 ml of 0.1 M  $\text{Na}_2\text{CO}_3$ , 20 ml of 0.1 M  $\text{NaHCO}_3$  in a closed flask separately, and agitating for 48 h at room temperature. Filtered and from that filtrate 5 mL was pipetted out and titrated with 0.1 M HCl<sup>20,21</sup>.

**Fourier transform infrared analysis:** Functional groups in FAN and FAN-MO were examined by using the FTIR method of analysis. The FTIR spectrophotometer was based on changes in dipole moment resulting from bond vibration upon absorption of IR radiation. It was carried out at room temperature using Spectrum RX1 "Pelmer" version 5.3 Spectrophotometer in the spectral range of 4000 to 400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

**Adsorption and kinetic studies:** A stock solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (1000mg/L) was prepared and suitably diluted accordingly to the various initial concentrations. Adsorption studies were carried out at room temperature ( $27 \pm 5^\circ\text{C}$ ). Batch adsorption studies were carried out using 0.2g of adsorbent for each bottle, the adsorption experiments were carried out with 50 mL of solution of required concentration and pH of the solutions varied from 2 to 10 in a bench shaker at a fixed shaking speed of 120 rpm. The resulting mixture was filtered (Whatmann filter paper No.41) and the initial and final concentrations of the metal ions were determined by UV-2450 vis spectrophotometer. The pH of the solution was adjusted using 0.1M HCl and 0.1M NaOH. The experiments were carried out for various adsorbent dosages, different initial Ni(II) ions concentration, for various contact time and different initial pH of the solution. The stock solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  was prepared for the concentration of 1000 ppm and it was diluted to various required concentrations. From the initial and final concentration, percentage removal can be calculated by

$$\% \text{ of removal} = \frac{(C_o - C_f)}{C_o} \times 100 \quad (1)$$

where,  $C_o$  - initial concentration of nickel in mg/L,  $C_f$  - final concentration of nickel in mg/L. The data obtained in batch mode kinetics were used to calculate the equilibrium metal uptake capacity. It was also calculated for adsorptive quantity of nickel by using the following expression:

$$q_e = \frac{v \times (C_o - C_e)}{w} \quad (2)$$

Where  $q_e$  is the equilibrium metal ion uptake capacity in mg/g,  $v$  is the sample volume in litre,  $C_o$  the initial metal ion concentration in mg/L,  $C_e$  the equilibrium metal ion concentration in mg/L and  $w$  is the dry weight of adsorbent in grams.

**Adsorption isotherms:** Equilibrium studies were undertaken to understand the behaviour of the adsorbent at an equilibrium condition. Equilibrium data are basic requirements for the design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the metal ion on to the adsorbent. The results obtained on the adsorption of nickel were analysed by the well-known models given by Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Harkin-Jura and Frenkel-Halsey-Hill isotherms. For the sorption isotherms, initial metal ion concentration was varied while the pH of the solution and adsorbent weight in each sample held constant. The sorption

isotherms were realized with FAN at solution pH 3 and FAN-MO for nickel at solution pH 5 for nickel ion adsorption. The experimental results were used for the calibration of parameters of the six adsorption isotherm are presented in table-1.

**Langmuir isotherm:** Langmuir model is the simplest theoretical model related to monolayer adsorption on the surface with finite number of available identical sites<sup>22,23</sup>. The linear form of Langmuir equation is derived as:

$$\frac{C_e}{q_e} = \frac{1}{Q_e K_L} + \frac{1}{Q_e} C_e \quad (3)$$

Where  $Q_e$  (mg/g) and  $K_L$  (dm<sup>3</sup>/g) are Langmuir constants related to adsorption capacity and rate of adsorption.

**Freundlich isotherm:** Freundlich isotherm expression is an empirical equation assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage<sup>24</sup>. The well-known logarithmic form of the Freundlich isotherm is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $K_F$  (mg/g) (l/mg) and  $1/n$  are the Freundlich adsorption constant and a measure of adsorption intensity.

**Tempkin isotherm:** Tempkin assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage. Its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy)<sup>25</sup>. The Tempkin isotherm has been used in the form of:

$$q_e = B \ln A + B \ln C_e \quad (5)$$

where  $B=RT/b$ ,  $b$  and  $A$ ,  $R$  and  $T$  are the Tempkin constant related to heat of sorption (J/mol), equilibrium binding constant (l/g), gas constant (8.314 J/mol K) and absolute temperature (K).Dubinin-Radushkevich isotherm.

The D-R model was applied to estimate the porosity, apparent free energy and the characteristics of adsorption<sup>26-28</sup>. The D-R isotherm does not assume a homogeneous surface or constant adsorption potential. The D-R model has commonly been applied in the following equation (6) and its linear form can be shown in equation (7)

$$q_e = Q_m \exp(-K\varepsilon^2) \quad (6)$$

$$\ln q_e = \ln Q_m - K\varepsilon^2 \quad (7)$$

where  $K$  is a constant related to the adsorption energy,  $Q_m$  the theoretical saturation capacity,  $\varepsilon$  the Polanyi potential, calculated from equation (8)

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad (8)$$

The slope of the plot of  $\ln q_e$  versus  $\varepsilon^2$  gives  $K$  (mol<sup>2</sup>/(kJ<sup>2</sup>)) and the intercept yields the adsorption capacity,  $Q_m$  (mg/g). The mean free energy of adsorption ( $E$ ), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, was calculated from the  $K$  value using the following relation<sup>29</sup>. From the value of  $E$ , the adsorption mechanism was predicted.

$$E = \frac{1}{\sqrt{2K}} \quad (9)$$

**Harkin -Jura adsorption:** The Harkin-Jura adsorption isotherm can be expressed as

$$\frac{1}{q_e^2} = \left(\frac{B_2}{A}\right) - \left(\frac{1}{A}\right) \log C_e \quad (10)$$

where  $B_2$  is the isotherm constant.  $1/q_e^2$  was plotted vs.  $\log C_e$ . This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution<sup>30</sup>.

**Frenkel-Halsey-Hill isotherm:** The Frenkel-Halsey-Hill isotherm can be expressed as

$$\ln q_e = \frac{1}{n} \ln K - \frac{1}{n} \ln C_e \quad (11)$$

$\ln q_e$  was plotted vs.  $\ln C_e$ . This isotherm explains the multilayer adsorption by the existence of a heterogeneous pore distribution of the adsorbent<sup>31</sup>.

## Results and Discussion

**Characterization of adsorbents: Scanning electron microscopic studies (SEM):** The figure-1.a., 1.b and figure-2 clearly shows that the SEM was employed to observe the physical morphology of the FAN and FAN-MO at 1000 X magnification. The SEM images shown in figure-1, a clearly show that finer fly ash particles are primarily spherical, whereas the alkali treated fly ash particles shown in figure-1.b are mainly composed of irregular and porous particles in FAN and the FAN-MO, figure-2 shows the increased roughness of surface compared to fly ash and FAN.

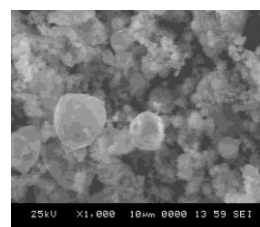


Figure-1a  
SEM image of fly ash

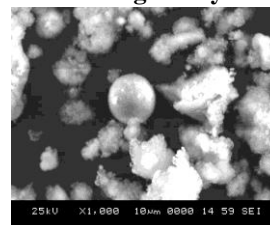
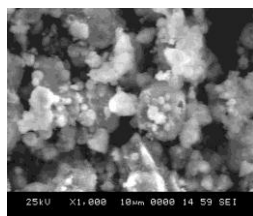
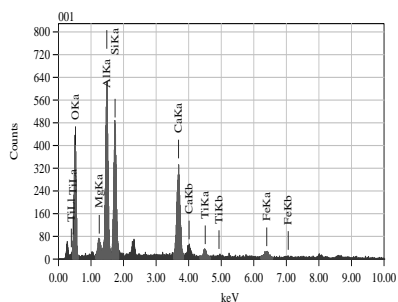


Figure-1b  
SEM image of FAN

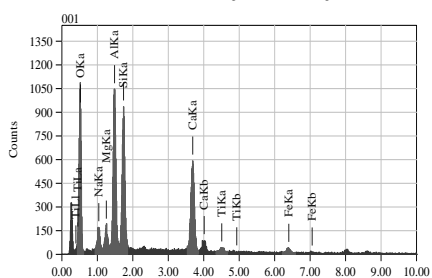


**Figure-2**  
SEM image of FAN-MO

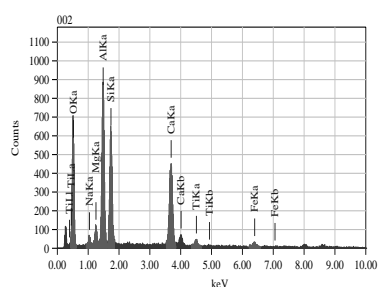
**Energy dispersive X-ray spectroscopic analysis (EDX):** The components of fly ash was SiO<sub>2</sub> 38.1%, Al<sub>2</sub>O<sub>3</sub> 36.36%, CaO 17.39%, MgO 3.28%, TiO<sub>3</sub> 2.55% and FeO 2.31%. The major components of FAN was SiO<sub>2</sub> 36.89%, Al<sub>2</sub>O<sub>3</sub> 33.04%, CaO 16.37%, MgO 4.77%, TiO<sub>3</sub> 1.38%, FeO 1.85 Na<sub>2</sub>O 5.71% and for FAN-MO was SiO<sub>2</sub> 33.76 %, Al<sub>2</sub>O<sub>3</sub> 38.36%, CaO 17.40%, MgO 4.99%, TiO<sub>3</sub> 1.73% and FeO 3.76% respectively. The presence of the above mentioned oxides in fly ash, FAN, FAN-MO are clearly shown in figure-3.a, 3.b and 4. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents make up about 70% of the fly ash. FeO and CaO contents compose about 19%.



**Figure-3a**  
EDX analysis of fly ash

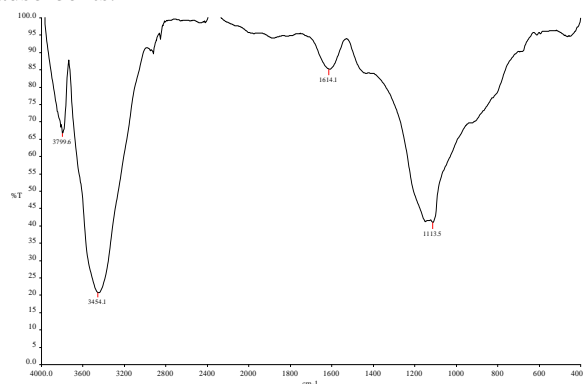


**Figure-3b**  
EDX analysis of FAN

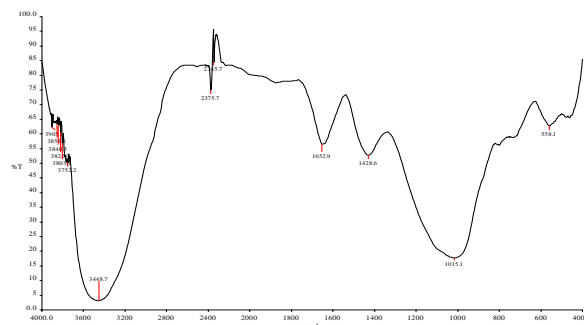


**Figure-4**  
EDX analysis of FAN-MO

**FTIR spectroscopic studies:** Surface functional groups were detected by Fourier transform infrared (FTIR) spectroscopy from the scanning range (4000 cm<sup>-1</sup>-400cm<sup>-1</sup>) and elemental analysis was performed using an elemental analysis. FTIR spectra for FAN and FAN-MO shows broadband between 3454.1 and 3448.7 cm<sup>-1</sup> in figure-5a and figure 5b, respectively. This indicates the presence of hydrogen bonded OH groups such as water either OH groups either of clay minerals or phenolic groups. This stretching is due to both the silanol groups (Si-OH) and adsorbed water (peak at 3400 cm<sup>-1</sup>)<sup>32</sup>. The FTIR spectra of FAN indicated peak in the region of 1614 due to C=C or C=O aromatic ring stretching bands (aromatic carbon peaks) aldehydes and ketones. The band at 1428 cm<sup>-1</sup> may be due to aliphatic C-H stretching vibrations in FAN-MO. The FTIR of FAN-MO showed a transmittance at 1113.5 cm<sup>-1</sup> due to the vibration of the C=O group in lactones<sup>33</sup>. Additionally intense vibration at 558.2 cm<sup>-1</sup> for FAN-MO is attributed to clay and silicate minerals<sup>34</sup>. The strong presence of peaks associated with bounded water, 3799.6, 3854.6 and 3840.5 cm<sup>-1</sup>, indicates that exposure of hydrolysed silica to compressive stress increased water dissolution into the silica structure as hydroxyl, for FAN and FAN-MO as expected by theory respectively<sup>35</sup>. Although some interference can be drawn about the surface functional groups from FTIR spectra, the weak and broad bands do not provide any authentic information about the nature of the surface oxides. The presence of polar groups on the surface are likely to give considerable cation exchange capacity to the adsorbents.



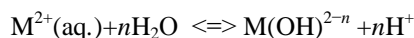
**Figure-5a**  
FTIR spectrum of FAN



**Figure-5b**  
FTIR spectrum of FAN-MO

**Acidity and basicity: (Boehm titration):** This titration shows the number of acidic, basic, phenolic, carboxyl and lactones sites. For FAN, the numbers of basic sites present were found to be 1.7 mEq/g. L, the numbers of phenolic, carboxyl and lactones groups were found to be 4.5mEq/g .L and the numbers of carboxyl groups present were found to be 2.44mEq/g.L. For FAN-MO, the numbers of basic sites present were found to be 1.8 mEq/g. L, the numbers of phenolic, carboxyl and lactones groups were 3.44mEq/g.L and the numbers of carboxyl groups present were 1.83 mEq/g. L. The above values for FAN and FAN-MO were also favourable for the possibility of ion exchange mechanism during the adsorption of Ni(II) process because the number of phenolic, carboxyl and lactones groups in FAN was higher compared to FAN-MO<sup>36-39</sup>.

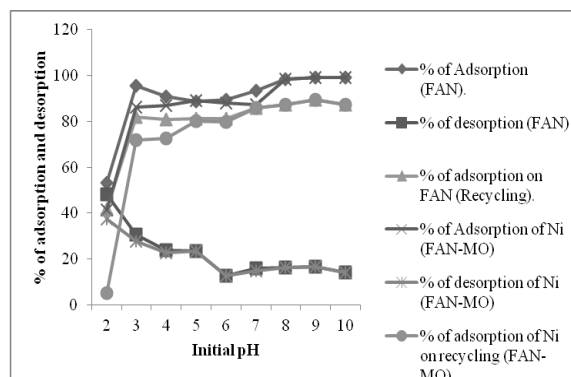
**Effect of pH on adsorption, desorption and recycling ability:** The pH of the solution has a significant impact on the uptake of heavy metals. The pH<sub>zpc</sub> of FAN was 2 and for FAN-MO, it was 4. The solution pH is above than the pH<sub>zpc</sub> of adsorbent, the surface of the adsorbent is highly loaded with negatively charged ion. It favours the adsorption of metal cation onto the negative surface of the adsorbent due to the electrostatic attraction. Therefore, it can be expected that positively charged metal ions are likely to adsorb onto the negatively charged adsorbents at a pH above ZPC for FAN and FAN-MO<sup>40</sup>. Metal cations in aqueous solutions hydrolyse according to the generalized expression for divalent metals.



The silica in FAN and FAN-MO could adsorb either positive or negative contaminants depending on the pH of the solution. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid, which can react with water, forming silanol (SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charge. The pH<sub>zpc</sub> of silica is generally in the neighbourhood of 2.0. Other solid material, such as iron and alumina, also shows the same phenomenon of developing positive or negative charges depending on pH. Iron as Fe<sub>2</sub>O<sub>3</sub> has a zero point charge 6.7, while that of alumina pH<sub>zpc</sub> equal to 8<sup>41-43</sup>. This indicates that the maximum Ni(II) ions adsorption capacity of FAN and FAN-MO can be attributed to the electrostatic interaction of the adsorbate with surface silica and iron sites of the adsorbents<sup>44-46</sup>.

Figure-6 indicates that the pH of the solution (2.0-10.0) had a significant effect on the adsorption of Ni(II) onto FAN and FAN-MO. At pH 3, the adsorptions of Ni<sup>2+</sup> on FAN and at pH 5, the adsorption of Ni<sup>2+</sup> on FAN-MO were found to be 95.41% and 89.2% respectively. Ni<sup>2+</sup> ions were removed by precipitation not in adsorption if the solution pH is above pH 8 for FAN as well as FAN-MO<sup>47</sup>. Thus, we fixed the pH 3 for FAN and pH 5.0 for FAN-MO in this study. As shown, the precipitation of the heavy metal ions except copper was less

than 20% at pH below 8, indicating that the removal of the metals except copper was mainly accomplished by adsorption below pH 8. Since the FAN has a low ZPC, the surface of the fly ash was negatively charged under the pH investigated. As pH increased from 3 to 8, it can be expected that the fly ash surface becomes more negatively charged. Thus, more favourable electrostatic attractive forces enhanced cationic metal ion adsorption as pH increased. However, the dependence of heavy metal adsorption on pH was different for each metal. The effect of pH on adsorption desorption and recycling capacities of FAN and FAN-MO for Ni<sup>2+</sup> removal in aqueous solution was given in the figure-6.



**Figure-6**  
**Effect of pH on adsorption and desorption of Ni(II) ions onto FAN and FAN-MO**

For FAN, the adsorption capacity increases initially to 95.41% until the pH reaches 3 and after pH 3, it decreases slightly, then increased and remained constant. But for FAN-MO, the adsorption capacity increased to 89.21% at pH 5 and decreased slightly, then increased to certain extent and remained constant.

In the wastewater treatment systems using adsorption process, the regeneration of the adsorbent and /or disposal of the loaded adsorbent are very important. Desorption studies were carried out for both the adsorbents FAN and FAN-MO by employing batch methods shown in figure-6. The maximum desorption of 48.29% took place in acidic medium at the pH 2 for FAN and 37.46% for FAN-MO at pH 2. The results indicate that nickel (II) ions adsorbed onto both FAN and FAN-MO can be recovered by distilled water which was higher for FAN compared to FAN-MO. After desorption the adsorbent were further used for adsorption process for the removal of Ni(II) ions. The percentage of removal of Ni(II) ions were found to be 81.89 % for FAN at pH 3 and 80.32% for FAN-MO at pH 5 given in figure-6. The increase in the removal of Ni(II) ions took place after pH 7 may be due to precipitation of metal ions in alkaline medium and not by adsorption.

**Effect of contact time:** Aqueous nickel metal ion solutions with initial ion concentration of 100mg/L were kept in contact with FAN and FAN-MO from 5 minutes to 60 minutes. The rate of removal was rapid for first 25 minutes for both the adsorbents

and thereafter the rate of metal removal attains equilibrium. No significant change in metal ion removal after 45 minutes for both FAN and FAN-MO. During the initial stage of adsorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to occupy due to repulsive forces between the adsorbate molecules on the solid surface. The maximum uptake of nickel metal ions at pH 3 for FAN were 95.41% and at pH 5, the maximum uptake of nickel metal ions were 89.21% at the equilibrium time of 50 minutes.

**Adsorption Kinetics:** The adsorption process of  $\text{Ni}^{2+}$  can be fitted well using the pseudo second order rate for both FAN and FAN-MO. The kinetic parameters were given in the table-1. The  $q_e$  value (25.44) obtained from second order kinetic equation for FAN was close to the experimental  $q_e$  value (21.1) and the linear regression coefficient value  $R^2$  value (0.9978) obtained for pseudo second order kinetics was close to unity compared to the  $R^2$  value (0.7694) obtained from first order kinetics. The values on initial sorption (h) that represents the rate of initial adsorption, is  $4.6 \text{ mg(gmin)}^{-1}$  for FAN. This indicates the adsorption of Ni(II) ions onto FAN follows pseudo second order kinetics. The  $q_e$  value (23.42) obtained from second order kinetic equation for FAN-MO was close to the experimental  $q_e$  value (19.33) and the linear regression coefficient value ( $R^2$  value 0.9947) obtained for pseudo second order kinetics was close to unity compared to the  $R^2$  value (0.5998) obtained from first order kinetics. The values on initial sorption (h) that represents the rate of initial adsorption, is  $5 \text{ mg(g min)}^{-1}$  for FAN-MO. This indicates the adsorption of Ni(II) ions onto FAN-MO follows pseudo second order kinetics.

The Elovich equation, the linear coefficient value for FAN was found to be 0.9547, where as it was 0.9032 for FAN-MO. Elovich constants  $A_E$  (desorption constant,  $\text{g mg}^{-1}$ ) and  $B_E$  (Initial adsorption rate,  $\text{mg(g min)}^{-1}$ ) for FAN were  $0.2647 \text{ mg/g min}$  and  $772.57 \text{ g/min}$  respectively. Elovich constants  $A_E$  and  $B_E$  for FAN-MO were  $0.3476 \text{ mg/g min}$  and  $7823.5 \text{ g/min}$  respectively. This value also best for FAN-MO compared to FAN, proves the applicability of Elovich equation for FAN-MO than FAN.

In intraparticle diffusion model, the values of  $q_t$  were found to be linearly correlated with values of  $t^{1/2}$ . The  $K_d$  values were calculated by using correlation analysis.  $K_d = 1.59 \text{ mg g}^{-1} \text{ min}^{-1/2}$ ,  $R^2 = 0.9005$ ,  $C = 12.445$  for FAN and  $K_d = 1.27 \text{ mg g}^{-1} \text{ min}^{-1/2}$ ,  $R^2 = 0.9453$ ,  $C = 12.36$  for FAN-MO were obtained using intraparticle diffusion model. The  $R^2$  values were found to be close to unity for FAN-MO compared to FAN, indicating the application of this model is best fitted to FAN-MO compared to FAN. This reveals the presence of intra particle diffusion process in FAN-MO than for FAN. The values of intercept C given in Table-1 provide information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase. The value of C for FAN was 12.445 and the value for C was 12.36 for FAN-MO.

**Effect of adsorbent dose:** The maximum adsorption capacities of FAN at pH 3 recorded as 95.41 % and 89.2% for FAN-MO at pH 5 for the dosage of  $0.2 \text{ g/50 mL}$ . This was increased to 98.55% for FAN and 96.88% for FAN-MO. This was due to the increase in the adsorption sites as increase the dose from 0.2g to 1g in 50 mL.

**Effect of Ni(II) ion concentration on adsorption:** The initial metal concentration provides an important driving force; hence a higher initial concentration of metal ions will increase the sorption rate. As the concentration of Ni(II) ions increased from  $25 \text{ mg/L}$  to  $200 \text{ mg/L}$ , the percentage of adsorption decreased. The percentage of adsorption for FAN was found be decreased to 85.32% and for the percentage of adsorption for FAN-MO was decreased to 80.49%. This was due to the increase in concentration of Ni(II) ions for lesser number of adsorption sites.

**Adsorption isotherm:** To optimize the design of an adsorption system for the adsorption of Adsorbate, it is important to establish the most appropriate isotherm model. Various isotherm equations like those of Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Harkin Jura and Frenkel Halsey isotherm have been used to describe the mono-component equilibrium characteristics of adsorption of Ni(II) ions onto FAN and FAN-MO. The experimental equilibrium adsorption data were obtained by varying the concentration of Ni(II) ions with fixed dosage of FAN and FAN-MO. The adsorption parameters for each metal ion obtained from the fitting of different isotherm models with the experimental data are listed in Table-2 along with the linear regression coefficients,  $R^2$ . FAN and FAN-MO have a homogeneous surface for the adsorption of metal ions. Therefore, it is expected that the Langmuir isotherm equation can be better represent the equilibrium adsorption data. The  $R^2$  value is closer to unity for Langmuir model than that for the other isotherm models for both FAN ( $R^2 = 0.9995$ ) and FAN-MO ( $R^2 = 0.999$ ). Therefore, the equilibrium adsorption data of Ni(II) ion adsorption on FAN and FAN-MO was represented appropriately by the Langmuir model in the studied concentration range.

The calculated value of D-R parameters is given in Table-2. The saturation adsorption capacity  $Q_m$  obtained using D-R isotherm model for adsorption of Ni(II) ions onto FAN and FAN-MO is 22.32 and  $21.28 \text{ mg g}^{-1}$  at  $0.2 \text{ g 50mL}^{-1}$  adsorbent dose, which is close to that obtained (21.23 and 20.04) from Langmuir isotherm model given in Table-2 respectively. The values of E calculated using Eq. 8 is  $5 \text{ KJ mole}^{-1}$  and  $4.083 \text{ KJ mole}^{-1}$  for FAN and FAN-MO respectively, which indicating that the ion exchange mechanism was favourably taking place in the adsorption of  $\text{Ni}^{2+}$  ion adsorption onto FAN and FAN-MO (for Ion exchange mechanism the value of E was found to be within  $1.3$  to  $9.6 \text{ KJ mole}^{-1}$ )<sup>48</sup>.

**Column studies:** Breakthrough capacity curves are important in process design because they are directly related to the feasibility

and economics of a given process<sup>49</sup>. The time taken for elution is very less compared to batch mode studies where it took 50 minutes to attain equilibrium. Figure-7 shows that 50 mL of Ni<sup>2+</sup> ion solution(100 mg/L) of pH 3 for FAN and 50 ml of Ni<sup>2+</sup> ion solution(100mg/L) of pH 5 for FAN-MO could be passed through a column without any Ni<sup>2+</sup> ions being detected in the effluent when 0.2 g adsorbent used. The results obtained at 5 mL/min were calculated from the breakthrough curve. The retention time of the analyte (V<sub>R</sub>) determined as 41.5 ml for FAN and 31.7 ml for FAN-MO corresponding to the volume respect to the half the initial concentration<sup>50</sup>.

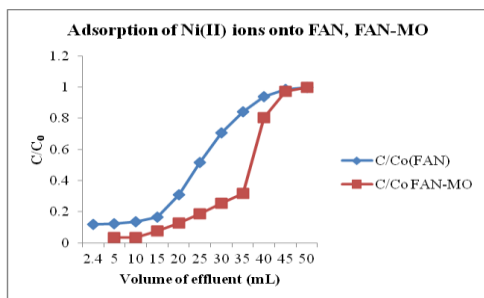


Figure-7

Break through capacity of FAN and FAN-MO

$$V_R = 0.5 (V_0) \quad (12)$$

The breakthrough volume (V<sub>B</sub>) is usually defined

$$V_B = V_R - 2\sigma_v \quad (13)$$

where  $\sigma_v$  is the standard deviation which can be determined graphically from the breakthrough curve.  $\sigma_v$  is in direct relation to the efficiency of the solid phase extraction column, the number of theoretical plates (N) which can be calculated from the breakthrough curve shown in figure-7 using the equation:

$$N = V_R (V_R - \sigma_v) / \sigma_v^2 \quad (14)$$

The capacity factor of the solute (k), can be calculated from the fundamental equation of chromatography:

$$k = \frac{V_R}{V_B} - 1 \quad (15)$$

The recovery factor 'r' can also directly related to the breakthrough curve. The recovery factor can be calculated by using the equation:

$$r = \frac{V_M k}{V_0} \times 100\% \quad (16)$$

where V<sub>M</sub> represents the hold up volume of the solid phase extraction cartridge. The parameters calculated by using the above relationships for both FAN and FAN-MO were given in the table-3.

For the desorption experiments, several solvents (acids, bases and water) have been used. Desorption with water was found to be 24.1% which was higher than for other desorbing agent used for FAN. Desorption with 0.1M HCl was found to be 62.22% higher than other desorbing agent for FAN-MO.

**Influence of other metals on adsorption of Ni(II) ions:**

Influence of Zinc (II) ions and Cu(II) ions on adsorption of Ni(II) ions. The concentration of Ni(II) ion solution was kept as 100 ppm. The concentration of Cu(II) ions were varied as 10, 20, 30 and 40 mg/L. Each solution was taken in the bottles and the pH was adjusted to 3 for FAN and after shaking 50 minutes, the percentage of adsorption was calculated. The percentage of adsorption decreased from 95.41 % to 83% as the concentration of Cu(II) solution increased in both the cases. This showed that there was a competitive adsorption taking place to certain extends between the Ni(II) ions and the Cu(II) ions. The same procedure was repeated for Ni(II) ions in presence of Zn(II) ions. The adsorption percentage of Ni(II) ions was decreased to 95.41% to 81.25% in presence of Zn(II) ions. The same procedure was repeated for FAN-MO at solution pH 5 and the adsorption was decreased to 89.25% to 79.06% in presence of Cu(II) ions. The adsorption percentage of Ni(II) ions was decreased to 89.25% to 80.86% in presence of Zn(II) ions.

**Influence of Zn(II) ions and Cu(II) ions on adsorption of Ni(II) ions:**

The concentration of Ni(II) ion solution was kept as 100 mg/L. The concentration of Zn(II) ion solutions and Cu(II) ion solutions were varied as 10, 20, 30 and 40 mg/L. Each solution was taken in the bottles, which were added to Ni(II) solution, and the pH was adjusted to 3 for FAN and after shaking 50 minutes, the percentage of adsorption was calculated. The percentage of adsorption decreased from 95.45% to 82.44% as the concentration of Ni(II) ions and Cu(II) ions increased. This showed that there was a competitive adsorption taking place to certain extends between the Ni(II) ions, the Zn(II) ions and Cu(II) ions. The percentage of adsorption of Ni(II) in presence of other metals was decreased. The same procedure was repeated for the adsorbent FAN-MO at pH 5 and the percentage of adsorption was decreased from 89.25% to 75.83%.

Table-1  
Comparison of kinetic parameters of Ni(II) adsorption on FAN and FAN-MO

Adsorbent	Pseudo-first-order equation				Pseudo-second-order equation				Elovich equation			Intraparticle diffusion		
	q <sub>e, cal</sub> (mg/g)	k <sub>1</sub> sec <sup>-1</sup>	q <sub>e, exp</sub> (mg/g)	R <sup>2</sup>	k <sub>2</sub> (Lmole <sup>-1</sup> sec <sup>-1</sup> )	h	q <sub>e, cal</sub> (mg/g)	R <sup>2</sup>	A <sub>E</sub> (mg/g min)	B <sub>E</sub> (g/min)	R <sup>2</sup>	kd (mg/g min <sup>1/2</sup> )	R <sup>2</sup>	C
FAN	13.49	0.082	21.1	0.7694	0.0072	4.6	25.44	0.9978	0.2647	772.57	0.9547	1.58	0.9005	12.45
FAN-MO	10.34	0.062	19.33	0.5998	0.0092	5	23.42	0.9947	0.3476	7823.5	0.9032	1.27	0.9453	12.36

**Table-2**  
**Isotherm constants and coefficients of determinations for FAN and FAN-MO**

Isotherm model	FAN	FAN-MO	Isotherm model	FAN	FAN-MO
Langmuir			Dubinin-Radushkevich		
$Q_m$ (mg/g)	21.23	20.04	$Q_m$ mg/g	2.32	21.28
$K_a$ (l/mg)	3.16	1.686	$K$ ( $\times 10^{-8}$ mol <sup>2</sup> /KJ <sup>2</sup> )	2	3
$R^2$	0.9995	0.999	$E$ (kJ mol <sup>-1</sup> )	5	4.083
			$R^2$	0.1083	0.349
Freundlich			Harkin-Jura		
1/n	0.0259	0.0384	$R^2$	0.9252	0.792
$K_F$ (mg/g)	23.65	23.56	A	2500	2500
$R^2$	0.5363	0.8087	B	4.5	4.5
			$q_e$	26.83	27.52
Tempkin			Frenkel -Halsey		
$\alpha$ (l/g)	36.76	23.35	$R^2$	0.5363	0.8087
$\beta$ (mg/l)	0.5761	0.8276	1/n	0.0259	0.0383
b	4372.8	3043.9	K	$1.1 \times 10^{53}$	$6.69 \times 10^{35}$
$R^2$	0.5292	0.8162			

**Table-3**  
**The parameters calculated for FAN and FAN-MO for adsorption of Ni(II) ions**

Parameters	% of adsorption	VB (ml)	VR (ml)	VM (ml)	N	r%	% of desorption			
							HCl	Water	NaOH	K
FAN	57.4	0.1	41.5	2.4	2.01	84.8	9.5	24.1	24.8	16.3
FAN-MO	96.56	0.7	31.7	4	2.14	55.4	62.22	32.1	8.26	16.93

## Conclusion

Treating the fly ash with alkaline NaOH (4N) solutions, the surface is modified by dissolution and reprecipitation reactions. By dissolution of acid oxides, the specific surface area is enhanced and activated and the efficiency of heavy metal removal increases. Adding dye to the fly ash surface results in a new surface, which is one more homogeneous but less negatively charged. The overall effect is a decrease in the affinity for heavy metals.

The adsorption of Ni(II) ions is pH-dependent with maximum adsorption of 95.45% occurring at pH 3 for FAN and 89.25% for FAN-MO at pH 5. The adsorption data was well fitted by the Langmuir isotherm model which shows monolayer adsorption capacity of FAN and FAN-MO. Adsorption of Ni(II) ions onto FAN and FAN obeyed pseudo second order kinetics. The adsorption of Ni(II) ions can be desorbed from both the adsorbents using water was 48.29% of adsorbed Ni(II) ions from FAN and 37.46 % of adsorbed Ni(II) ions were recovered from FAN-MO by batch mode studies at pH 3. The percentage of adsorption of Ni(II) ions on FAN and FAN-MO was slightly

higher in single system than binary and tertiary system which shows the competitive adsorption between the metal ions. Compared to FAN-MO, FAN had higher adsorption ability for the removal of Ni(II) ions from aqueous solution. In column studies, the removal efficiency of Ni(II) ions were less compared to batch mode studies for both FAN and FAN-MO, but the time taken for adsorption was only 10 minutes. With these conditions, we found the column study was not much suitable compared to batch mode studies for removal of Ni(II) ions onto FAN and FAN-MO. The experimental results show that this can be an up-scalable solution and represent a step in investigating the process of complex treatment of wastewater containing dyes and heavy metals.

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