The Adsorption Efficiency of Modified Fly Ash for the Removal of Iron and Zinc Ions

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Abstract: The aim of study was to reduce chemical contaminant from water and wastewater by adopting low-cost adsorption process over modified fly ash, which prepared easily by two methods, alkaline added under hydrothermal conditions, some physio-chemical technique used to characterize the modified fly ash as XRF, XRD, BET technique and scanning electron microscopy SEM. The result showed that the modified fly ash has crystal structure hexagonal and it attributed to zeolite A, the regarding of crystal structure, specific surface area and external morphology examined by SEM, the estimation of specific surface area affiliated to type (IIB) isotherm which is similar to non-porous or macroporous materials, finding results showed that the modified fly ash described better to both Freundlich and Langmuir model isotherm for removal mechanism, the maximum adsorption capacity q_{max} for Zn^{2+} an Fe^{2+} is 114.2 and 196.7 mg/L respectively, furthermore, iron and zinc ions removed well by direct method SZ1 due to the crystal lattice structure, big surface area and pore size 49.317 and 38.813 m^2/g respectively, finally modified fly ash can be used as low-cost adsorption material due to the nature of ion-exchange and performance in adsorption according to their big surface area.

Keywords: Fly Ash, Modified Fly Ash, Adsorption, Isotherm, Marco-porous

1. Introduction

Over the coming decades demand for freshwater and energy will be raised due to meet the need of fast increasing growing of population and economies, this will load on limited natural resources. There are many sources to generate electricity power, one of the broad uses is thermal power generation, which using coals, natural gas, oil, fossil fuel and petroleum coke [1].

The power station product coal fly ash CFA during electricity generation at 1200 -1700°C, various compound organic and inorganic identified, Blisset et al investigated that more than 316 individual minerals and 188 mineral group existed in different CFA. [2]. fly ash consider to be byproduct from coal combustion, the landfill of CFA affects the environment especially ground water and surface water, in the other hand the important beneficial is to convert this waste to sustainable material, therefore, in 2012 United

States produced alone 52 million tons of CFA about 45% of total products of CFA in the world [3], more than 85% of most fly ashes contain chemical compounds and glasses, the chemical composition rich of metal oxide such as $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O > Na_2O > TiO_2$, form moderate to high concentrations [2], [4]. Ramezani identified that North America is the first country used fly ash in concrete in early 1937 from that time CFA became a major component to facilitate concrete, however, it can improve the feature of concrete by reducing the carbon footprint [4].

The main constituents in CFA are silica and Alumina which can be converted easily to zeolite by two methods hydrothermal and fusion. Fusion method restricted by speed of reaction, however, the final production depends on some conditions such as suitable range of temperature as well as promoting agent like sodium hydroxide or potassium chloride to enhance the reaction activity by increasing crystalline formation. In last few years fly ash has been used in wild range as raw materials, low cost microporous

aluminosiliceous as zeolite to remove heavy metals, anions groups, and other metals ions, due to its unique function big surface area, suitable pore size and volume by adopting ion exchange and adsorption technique [5]

The term zeolite received attention in last few years due to unique structure it's highly crystalline alumina-silicate materials Si and Al are major components they form SiO_4 and AlO_4 structure, it can reduce and recovery some element ions from their solutions easy by adsorption and ion exchange technique, however, can be used in catalysis as carrier materials, zeolite A was prepared first in 1954 Pathak achieved that in 2014 [6]. A types of zeolite have been prepared from fly ash such as zeolite type 4A, X type, Y type and MCM-41 [7-9]. It should be noted that, indirect methods haven`t been used in wild range.

Heavy metals have harmful effect in environment and human, the concentration of heavy metals increase due to some industrial especially electronic industries, cooling systems and plating industry, organic wastes and ground water, it exists in water, soil, and air, heavy metals react with cellular structural proteins, enzymes and membrane system, certain metals such as chromium and nickel have been linked with cancers in exposed human populations, whereas heavy metals have some benefit such as zinc deficiency is associated with poor growth and development and impaired immune response also iron it can a bear in anemia [10-12].

Modified fly ash synthesized in the present study by two methods direct and indirect and physiochemical characterization and the efficiency performs to remove Zn^{2+} and Fe^{2+} from aqueous solution has been studied

2. Experimental

Flay ash collected from Garri electricity station (North Khartoum- Sudan). Fly ash is by- product of thermal electricity power station which consume petroleum cock, Seliman et al estimate the function and the properties of petroleum cock [13].

The XRF analysis estimated chemical composition of the fly ash consists mainly of Silica and Alumina as a major, other metals oxide such as Fe_2O_3 and CaO occurring as minor, the element parentage in fly ash samples was found to be as in Table 1.

Table 1. Fly ash composition.

Metal oxide	percentage
SiO_2	39.8
Al_2O_3	25.9
Fe_2O_3	16.8
CaO	1.98
TiO_2	0.84
Unburnt carbon	33.24

The collected samples were initially screened to eliminate larger particles and calcined at $800 \pm 10°C$ for 2 h to remove the unburnt carbon and volatiles. The syntheses of zeolite from fly ash was followed according to the procedure reported by Ruen-ngam et al [14, 9], direct methods prepared

by added alkali to fly ash under following step. 10 g of fly ash was added to 10 g of sodium hydroxide, the mixture was burnt in air at 550°C for one hour in furnace, the product was crushed and dissolved in 85 cm^3 distilled water then stirred for 25 hours at room temperature, the crystallization started, after placed on autoclave for 2 hours at 90°C. The final product was washed several times with distilled water until the pH reached 10 and it was dried over night at 105°C labeled as SZ1. While, indirect type of zeolite was prepared by treating fly ash with 2M sodium hydroxide with 3:1 ratio, heated to boil for 2 hours, however, the extract solution neutralized by 1 M HCl, white gel obtained after few minutes, under stirring at room temperature, whereas white gel saved in autoclave for 10 hours, then it washed and calcinated at 600°C for 2hours labeled as SZ2.

2.1. Characterization and Analysis

X-ray diffraction XRD used to indicate crystalline as well as purity and structure, the samples were grounded into fine homogenous powder and exposed to X-ray. The wild angle x-ray scattering of samples was measured by X-ray diffraction (D8 advanced powder diffractometer) with Cu Kα radiation, the diffraction was collected at 5-90° with step size of 0.028°, while CaF_2 used as internal standard, the technique done by using (Panan analytical X'Pert³ MRD (Netherlands)), however, chemical composition of the samples was analyzed by X-ray Fluorescence XRF. On the other hand the specific surface area, pore size, and volume were calculated using the adsorption of data of N_2 (adsorption-desorption) analysis by adopting Brunaur, Emmett and Teller (BET) model in the relative pressures range between 0.05 to 0.35, whereas the distribution of the pores and their average diameter were calculated from the BJH model. In addition the surface area and morphology determined by scan electron microscopy SEM Shematzu Japan, monograph image of aforementioned samples were taken on 500μ magnification. The concentration of remaining metals determined by atomic absorption spectroscopy using the standard procedure, by (Savanta serial No AA7638GBC (Australia).

2.2. Physical Properties

The samples were grounded and sieved in the mesh between 150 to 200 μm, although the mechanisms of zeolite as cation exchange is participating ion through the internal channels and cavities or their hindered movement through the film of ordered water which exists on the surface of the zeolite. Although to indicate ion exchange capacity of the samples, convert final product (zeolite) to NH_4-zeolite by added 0.1M NH_4Cl for 2 hours, filtration and determined the concentration of NH_4Cl in the solution, ion exchange capacity confirmed [15].

2.3. Adsorption Isotherms

The equilibrium adsorption of Fe^{2+} and Zn^{2+} ions in to modified fly ash carried out by contacting 0.5 g adsorbent with 50 cm^3 ionic solution at different concentration from 100 to

500 ppm for 80 minutes in starrier, in constant temperature and pH, the filtrate was analyzed by atomic absorption (AAS), while the amount of adsorbed qe (mg/g) was calculated by using Vanderborght and Van Griekenn formulation

$$q_e = \frac{V(C_0 - Ce)}{m} \tag{1}$$

Where (q_e) is the metal concentration on the zeolite (mg/g) at equilibrium, (C_e) is metal concentration in solution (mg/dm^3) at equilibrium, (C_o) is initial metal concentration in solution (mg/dm^3), (V) is initial volume of metal solution used (cm^3), and (m) is mass of zeolite used.

Equilibrium data, commonly known as adsorption isotherms, are a requirement for design an adsorption system, there are many adsorption models such as (Freundlich, Langmuir, and Dubinin- Radushkevch …. etc.).

Freundlich and Langmuir were used to describing the equilibrium between adsorbed metals ions on the samples cell (q_e) and metals ions in solution (C_e) at a constant temperature. Freundlich model supposes that uptake or adsorption of ions occurs on the heterogeneous surface by monolayer, these data often fit the empirical equation proposed by Freundlich:

$$q_e = K_f(C_e)^{\frac{1}{n}} \tag{2}$$

Where K_f and n are constant of Freundlich characteristic of the system used to indicate the capacity and intensity of adsorption.

Equation (1) can be linearized in logarithmic form and the constants can be determined, to find (n) and (k) plot log C_e vs log q_e.

$$Log(q_e) = LogK_f + \frac{1}{n}Log(C_e) \tag{3}$$

Where K_f and 1/n are Freundlich constant due to adsorption capacity and adsorption intensity respectively, the value n determine the degree on nonlinearity between adsorption and concentration of the solution as:

n=1 adsorption is linear, n<1 adoption follow the chemical process, n> 1 follow the physical process.

Whereas, the Langmuir equation was described the metal ions on homogenous surface adopted by monolayer adsorption is given by Equation (4)

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{4}$$

q_{max} (mg. g^{-1}) is the maximum amount of metal ions per unit weight of solid to form a complete monolayer on the surface-bound

C_e = the equilibrium concentration of adsorbate (mg/L^{-1})

q_e = the amount of metals adsorbed per gram at equilibrium (mg.g^{-1})

K_L = Langmuir isotherm constant (L.mg^{-1})

To find Langmuir adsorption parameters transforming the equation (4) into leaner form

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \tag{5}$$

The value of q_{max} and K_L were calculated from the slope and intercept directly after the Langmuir plot 1/C_e vs 1/q_e. [16-18].

3. Results and Discussions

3.1. Physical Properties

The table shows the main physical properties of SZ1 and SZ, the result shows that SZ1 has a high ion exchange capacity than SZ2 as well as pore volume, pore diameter, and low moisture content.

Table 2. *Physical properties of the samples.*

Parameters	SZ1	SZ2
Cation exchange capacity meq g^{-1}	2.4	2.03
Particle size μm	150-200	150-200
Moisture content%	13	12
Surface area m^2/g	40.317	30.813
Volume pore cm^{3}g^{-1}	0.11	0.101
Pore diameter nm	1.17	1.12

3.2. Chemical Characterization

XRD results of the samples indicted the appearance of the crystal grain, the samples composted of quartz and iron oxides which located in the outer surface, the result showed slight different between SZ1 and SZ2 which indicate that both SZ1 and SZ2 points to hexagonal structure and four diffraction peaks were SZ1 observed at *2θ*= 20.77°, 26. 61°, 36.5°, and 50, SZ2 sample showed characteristic peak at *2θ* = 20.79°, 26.59°, 36.50° and 50.11°, while the d-spacing d$_{hkl}$ of SZ1 is 4.27, 3.34, 2.46, and 1.82 *Å* for SZ2 is 4.27, 3.35, 2.46, and 1.820 *Å*. The XRD pattern of the samples shows the pure-form and high crystalline structure, for these perspectives the samples attributed to zeolite A also known as LTA. Another way, fly ash prepared by Fronus et al by controlling the concentration of sodium hydroxide over fly ash, three types of zeolite were observed during synthesis Na-X, Na-Pi and sodaite [19, 20]
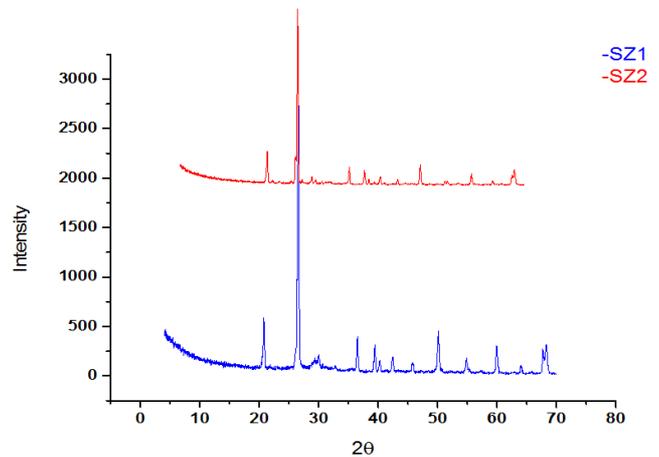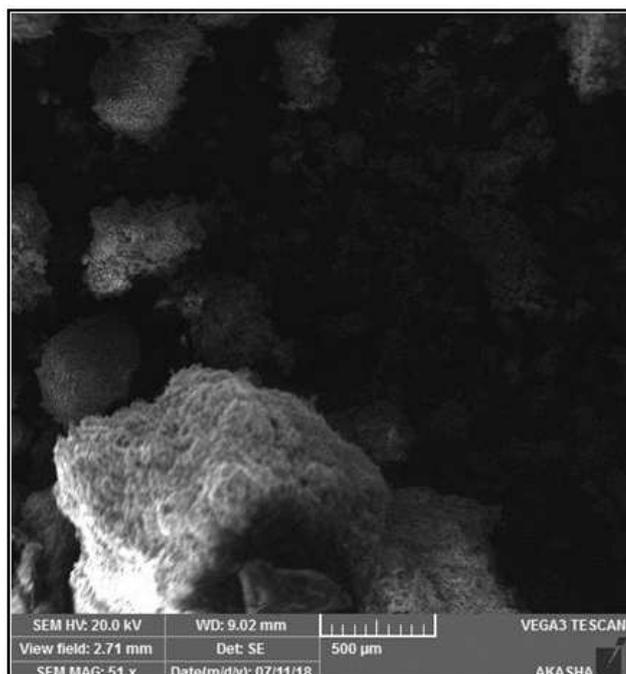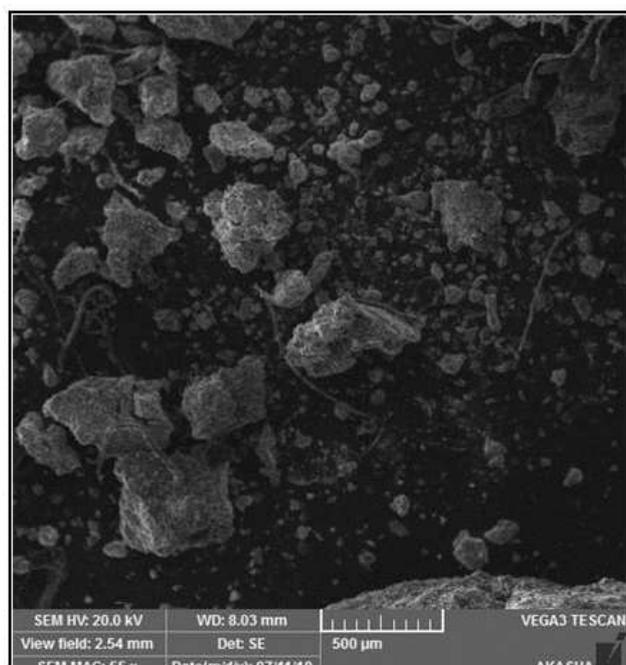

Figure 1. *XRD pattern of SZ1 and SZ2.*

information about physisorption mechanism which can predict the pre-type, the samples were classified as type ПB according to IUPAC classification, and for the samples, there is different of pore size combined. The type ПB normal for materials with non-porous or macroporous Aluminosilicate adsorbent, however, obtained monolayer and multilayer adsorption mechanism of gas, with an open and stable external surface of the samples. Nevertheless, the presence of the sharp sorption step adsorption start from 0.66 to 0.92 value of P/P_0 revealed that the samples resemble to macroporous. In addition the initial part of this type isotherm attributed to both mono and multilayer adsorption, the samples showed type H_3 of adsorption hysteresis loop which doesn`t exhibit any limiting adsorption at high P/P_o, the shape of the samples resemble zeolite A. [21, 9, 22]
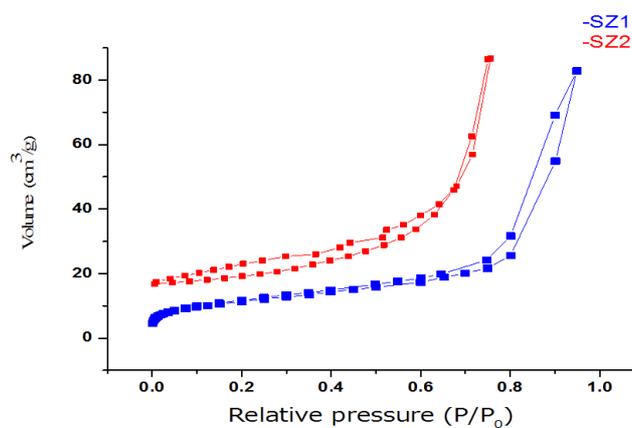

Figure 3. N_2 adsorption–desorption isotherm of SZ1and SZ2.

To understanding adsorption process and equilibrium condition, two types of isotherm applied, the isotherm adsorption of Fe^{2+} and Zn^{2+} over modified fly ash sieve were illustrated according to Freundlich and Langmuir, which they are most common isotherms for determining adsorption mechanisms process. Since n value on Freundlich isotherm for Zn^{2+} and Fe^{2+} lies < 1 is favored to fit physical adsorption on the surface of adsorbent where showed in Table 3, although, the value of n, when fallen between 1 to 10, represent good adsorption, while low value of n describe heterogeneity adsorbed ions on the adsorbent, for both SZ1and SZ2 K_f value fit between 0.57 and 1.8 [23]. The monolayer homogenous adsorption capacity saturation at equilibrium represented by Langmuir constant q_{max}, which for Zn^{2+} an Fe^{2+} is 114.2 and 196.7 mg/L respectively, the other constant K_L is used to indicate the affinity of ions Fe^{2+} and zn^{2+} to adsorbent. The result shown that SZ1 fit well to Freundlich isotherm according to the value of R^2 0.810 and 0.928, while, SZ2 plot high Langmuir than Freundlich isotherm due to R^2 value 0.924 and 0.998 which suggesting homogenous distribution surface, the ions Zn^{2+} and Fe^{2+} bent to the adsorbent by chemical bonds. [17, 24], however, the results exanimated the ability of these isotherms to described the process of adsorption in the solution, the parameters, and factors of the isotherms presented in Table 3 below.

Figure 2. SEM of SZ1 and SZ2.

The image of aforementioned samples by SEM in Figure 2 a and b revealed that the external morphology, well- defined crystal to both samples, was a hexagonal system, while the image showed external surface area, and the porous clear observed through SEM.

Nitrogen adsorption- desorption isotherm illustrated in Figure 3, however, the BET surface area of the samples 40.317 and 30.813 m^2g^{-1} respectively 5. The BET adsorption-desorption isotherm and its hysteresis loop give useful

Table 3. Isotherm parameters of SZ1 and SZ2 Freundlich an Langmiur.

	Ions	K_f	n	R	$q_{max\ mg/g}$	$K_{L\ mg/L}$	R	The equation
SZ1	Zn^{2+}	1.8	0.78	0.810	114.2	0.05	0.874	y = 0.6287x − 0.786 y = 0.0052x − 1E-05
	Fe^{2+}	1.02	0.42	0.928	196.7	0.03	0.952	y = 0.5485x − 0.4259 y = 0.0079x − 3E-05
SZ2	Zn^{2+}	1.7	1.7	0.972	0.15	0.00	0.924	y = -1.4574x + 1.7011 y = 0.0294x − 0.001
	Fe^{2+}	0.57	0.57	0.995	0.02	0.00	0.998	y = 0.8431x + 0.5762 y = 0.2931x + 0.0069

*The first equation belong to Freundlich isotherm

4. Conclusions

Heavy metal ions such as Zn^{2+}, Fe^{2+}, Cd^{2+} ……etc. have a harmful effect on the environment, it transfers into food network, they are persistent toxic in high concentration, and non-biodegradable metal. Through this study it found that treated fly ash by alkali under hydrothermal conditions has capable to enhance its adsorption capacity and therefore its removal efficiency, Zeolites is low-cost materials for water and waste water treatment due to their high ion exchange capacity and high-performance adsorption of cations in aqueous solution. Further understanding the effect of alkali treatment on the surface of fly ash, characteristics and properties of SZ1 and SZ2 were achieved through advanced characterization such as XRF, XRD, SEM, and BET specific surface area. The result shows that modified fly ash has unique structure, and high efficiency to reduce heavy metals from aqueous solutions, the removal equilibrium obey Langmuir isotherm for SZ2 while Freundlich isotherm fit well to SZ1, to sum up, the final product characterized by (XRD, BET method), it have big surface area as well as suitable pore size, it can use for catalysis design.

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