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Adsorption of Heavy Metals from Steel Processing Effluent on Sodium Hydroxide Modified Nigerian Kaolinite

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ABSTRACT

This study investigated the quality level of heavy metal-laden effluent discharge (wastewater) from a steel processing plant in Ilorin, Kwara State, Nigeria and the utilization of NaOH treated Nigerian kaolinite clay as low-cost adsorbent for remediation of the effluent. Physicochemical analysis of the wastewater was carried out and the clay adsorbent was characterized using X-Ray Diffractometry (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy coupled with Electron Dispersive Spectroscopy (SEM/EDS). From the results obtained, XRD reflection peaks of the 63 μm fractions obtained after purification revealed the clay as kaolin. FTIR absorption bands at 3689.64 and 3619.67 cm^{-1} represent surface -OH stretching of the octahedral and inner -OH between the tetrahedral and octahedral sheets. The EDS spectra of the kaolin following treatment with NaOH showed an increase in silica and alumina content from 15.92% to 24.81% and 13.36% to 15.58% respectively. Physicochemical parameters of the raw effluents were above the recommended limits set by National Environmental Standards and Regulations Enforcement Agency (NESREA) of Nigeria for industrial discharge. The metal ion concentrations were 309.0, 20.50, 40.40 and 10.90 mg/L for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions respectively. Successive reuse of the treated clay in four adsorption cycles recorded removal efficiency of 99.77, 99.95, 98.91 and 99.91% for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions respectively and decrease in the physicochemical parameters to permissible level. The Water Quality and Metal Pollution Indices (WQI/MPI) of the effluent after adsorption showed the treated wastewater fulfilled environmental requirement for industrial discharge. The study concluded that NaOH treated clay offered potential for remediation of heavy metal-laden industrial effluents.

Keywords: Adsorption, Clay, Effluents, Heavy metals, Steel

INTRODUCTION

Effluents from steel processing industries contribute greatly to contamination of water bodies. In general, steel processing industries deal with manufacturing of products including nail shanks, umbrella nail, reinforcement concrete mesh wire, binding wire, drawn wire and straightening wire. Roll bands of metal sheets processed into these products are treated in series of acid prickle bath to remove rust before lubrication for rust prevention (Harika *et al.*, 2015). These treatments result in generation of wastewater with high degree of acidity, suspended and dissolved solids, heavy metals, oil and grease and other organic pollutants. Heavy metals are the predominant contaminants in steel processing wastewater with concentrations at toxic level in most cases (Joyoti, 2013; Harika *et al.*, 2015).

Several physical, chemical and biological methods such as chemical oxidation, precipitation, adsorption on to different matrices, ozonation, solvent extraction, electrolysis, membrane filtration and activated sludge have been used for effluent treatment (Fu and Wang,2011; Joyoti, 2013). However, some of these techniques are considered too expensive, require high energy consumption or are rendered ineffective by the presence of recalcitrant contaminants (Smith *et al.*, 2012; Lin *et al.*, 2013). To overcome limitations and improve the efficiency of treatment process, some of the techniques considered compatible have been integrated as dual or multi-step complementary methods (Zhang *et al.*, 2012). Adsorption is a low-cost method of wastewater treatment and the effectiveness of clay minerals as adsorbent is well-established (Jiang *et al.*, 2010; Olaofe *et al.*, 2015; Emam *et al.*, 2016).Application of some chemically modified clay minerals as adsorbents have proven to be an effective method of heavy metal remediation from aqueous solutions of heavy metal ions. Modification of clay adsorbents with some alkaline, organic and inorganic acids and quaternary ammonium compounds are known to enhance the adsorption capacity of clays (Cruz-Guzman *et al.*, 2006; Al-Harahsheh *et al.*, 2009; Addy *et al.*, 2012). Weight Arithmetic Water Quality Index method has been designed to rate the quality of different sources of drinking water as shown in Table 1 (Tyagi *et al.*, 2013; Boah *et al.*, 2015).

The use of different adsorbents for remediation of heavy metal-laden industrial effluents have been reported. Examples include, removal of nickel from electroplating rinse water using coir pith and modified coir pith (Ewecharoen *et al.*, 2008), adsorption of heavy metals from electroplating wastewater on wood saw dust (Sciban *et al.*, 2007) and olive stone (Martin-Lara *et al.*, 2014). Acid-modified montmorillonite has effectively been used for remediation of automobile effluent (Akpomie and Dawodu, 2016).This study focused on the analysis of physicochemical parameters of acid pickle liquor discharge from a steel processing plant and the utilization of NaOH modified Nigerian kaolinite clay as a low-cost adsorbent for removal of Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions from the wastewater. To evaluate the economic viability of the adsorption process, the spent modified clay was regenerated and reused for successive adsorption of the effluent. The effectiveness of the clay to remove the metal ions and other contaminants was determined using Water Quality and Metal Pollution Indices.

Table 1: Water Quality Index

WQI Value	Water Quality Rating
0-25	Excellent water quality
26-50	Good water quality
51-75	Poor water quality
76-100	Very Poor water quality
Above 100	Unsuitable for drinking purpose

Source: Tyagi *et al.* (2013) and Boah *et al.* (2015)

MATERIALS AND METHODS

Preparation and Characterization of Clay Adsorbent

The natural clay sample (K-clay) was collected from Argungu deposit, Kebbi State; an extension of Sokoto sedimentary basin, Nigeria. Separation of the 63µm fraction particle size of K-clay from impurities was carried out using wet-sedimentation method (Ahmed *et al.*, 2012). The 63 µm fraction of the clay was treated with sodium hydroxide by adding 25.0 g portion of the natural clay sample to 500 mL of 0.2 M solution of NaOH and the suspension stirred with a magnetic stirrer at the rate of 200 revolutions per minute (rpm) for 60 minutes at 50^0C. The resulting slurry was centrifuged at 3000 revolutions per minute (rpm) for 30 minutes and the sediment washed repeatedly with deionized water to neutral pH and dried at 103^0C to give the NaOH modified kaolin (K-S clay).

Characterization of the clay was carried out using BRUKER, AXS D8 Advance X-Ray Diffractiometer (XRD), Bruker Tensor 27 Platinum ATR-FTIR and TESCAN VEGA TS 5136LM Scanning Electron Microscope coupled with Electron Dispersive Spectrometer (SEM/EDS).

Physicochemical Analysis of the Steel Effluent

Samples of the effluent were collected from a steel processing plant in Ilorin, Kwara state, Nigeria. Physicochemical parameters including pH, Electrical Conductivity (EC), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Dissolved Oxygen (DO), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Chloride and Sulphate ion content were determined using standard methods (Shun and Lee, 2004; De, 2012).

Adsorption of Heavy Metal Ions from the Steel Effluent

Adsorption of heavy metal ions on K-S clay was carried out by contacting the clay adsorbent with 0.25 L of the effluent. The experimental conditions were adsorbent particle size of 75 µm, pH range (3.0 -4.8), shaking speed 300 rpm, adsorbent dose 1.0 g/0.25 L, temperature of 55^0C and contact time of 240 minutes. Then, 5.0 mL samples were withdrawn using a syringe (hub packed with cotton wool) in the first 15 minutes and subsequently at time intervals of 30 minutes, centrifuged at 3500 revolutions per minute (rpm) for 15 minutes and the supernatant solution analyzed using Buck Scientific 210 VGP Atomic Absorption Spectrophotometer. After each adsorption cycle, the spent clay was regenerated through desorption by stirring with 0.2M HCl solution for one hour at 50^0C and then washed severally with deionized water before its reuse in successive adsorption cycles.

The adsorption capacity of K-S clay was determined using the mass balance equation;

$$q_x = \frac{V(C_i - C_x)}{W} \qquad (1)$$

Where C_i and C_x are the initial and final concentrations of heavy metal ions (mg/L), V is the volume of effluent (L), W is the weight (g) of adsorbent and q_x is the amount of heavy metals adsorbed at equilibrium (mg/g).

The percentage of heavy metal ions adsorbed was evaluated using the formula;

$$\text{Percentage removal } (\%) = \frac{(C_i - C_x) \times 100}{C_i} \qquad (2)$$

Weighted Arithmetic Water Quality (WQI) and Metal Pollution Indices (MPI) were used to evaluate the effluents quality before and after adsorption, following literature procedure (Tyagi *et al*., 2013; Boah *et al*., 2015).The results obtained were compared with permissible limits of the World Health Organization (WHO) and NESREA (2011). WQI and MPI indices were determined for the raw effluent and effluent after several cycles of adsorption with K-S clay.

RESULTS AND DISCUSSION

Characterization of the Clay

The following results were obtained from the characterization of purified 63 µm fraction of natural K-clay and portion treated with NaOH (K-S clay).

XRD Patterns:

The XRD patterns of K-clay showing the qualitative and quantitative mineralogical phase composition, confirm kaolinite as the only clay mineral present in the 63 µm fraction of the clay (Fig. 1). The reflection peaks for the interlayer spacing were predominantly observed at 2θ values of 12.4^0, 25^0, 38.5^0, and 62.5^0 respectively. Similar reflection peaks for kaolinite clay have been reported in literature: 12^0 and 25^0 (Emam *et al*., 2016) and 12.3^0, 19.8^0, 24.9^0 and 62^0 (Heah *et al*., 2013).

FT-IR:

The results of FTIR spectra obtained from the natural K-clay reveals triple hydroxyl group absorption bands in the IR region of 3600-3700 cm^{-1}which confirm the clay as kaolinite (Fig. 2). The two strong peaks at 3689.64 and 3619.67 cm^{-1} are associated with stretching of the surface hydroxyl groups of the octahedral layer and inner hydroxyl groups located in the plane between the tetrahedral and octahedral sheets. Nayak and Singh (2007); Jiang *et al*. (2009); Heah *et al*. (2013) reported values 3696.7 and 3622.5 cm^{-1}, 3695.9 and 3620.6 cm^{-1} and 3688 cm^{-1} and 3617 cm^{-1} respectively for the -OH groups. The third weak absorption band at 3651.57 cm^{-1} was assigned to out-of-plane stretching vibration hydroxyl group at the octahedral surface. Deformation band of water OH was observed at 1630 cm^{-1}.Si-O-Si stretching, in-plane Si-O stretching, Si-OH stretching and deformation bands of Al-Al-OH were observed at 1113.91, 1025.18, 999.05 and 909.68 cm^{-1} respectively. Two intensive peaks at 749.17 and 788.44 cm^{-1} correspond to Al-O and Si-O out of plane respectively. Al-O-Si bending vibration and Si-O-Si assignments were also observed at 525.01 and 458.66 cm^{-1} respectively. The values of absorption bands between the IR regions of 1630-400 cm^{-1}are similar to those reported in literature (Osabor *et al*.,2009; Djomgoue and Njopwouo, 2013).

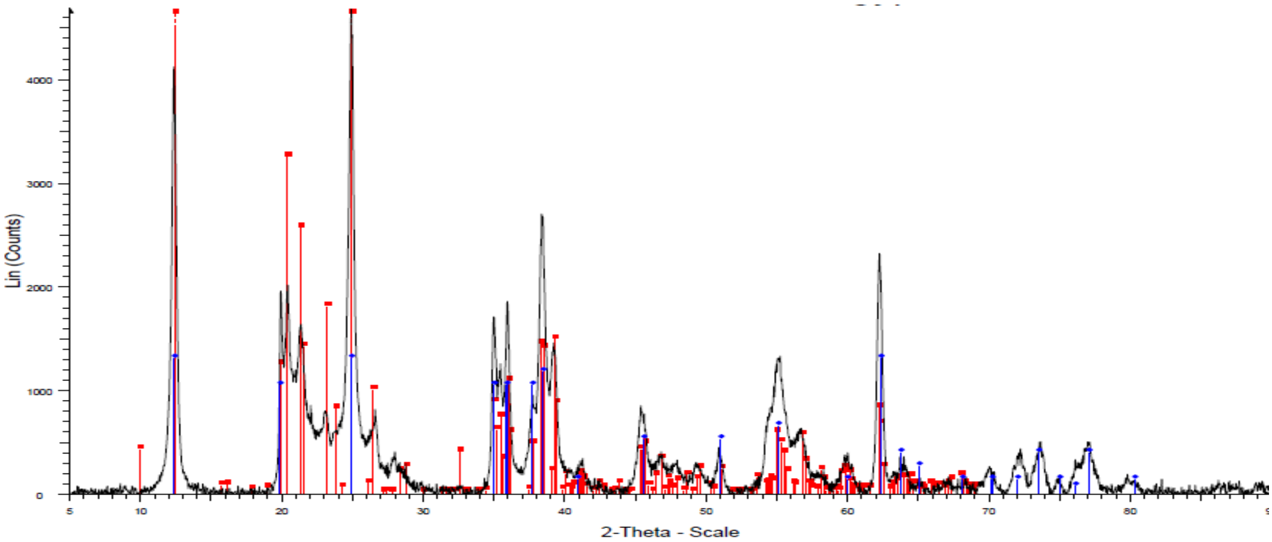

Fig. 1: XRD patterns of K-clay

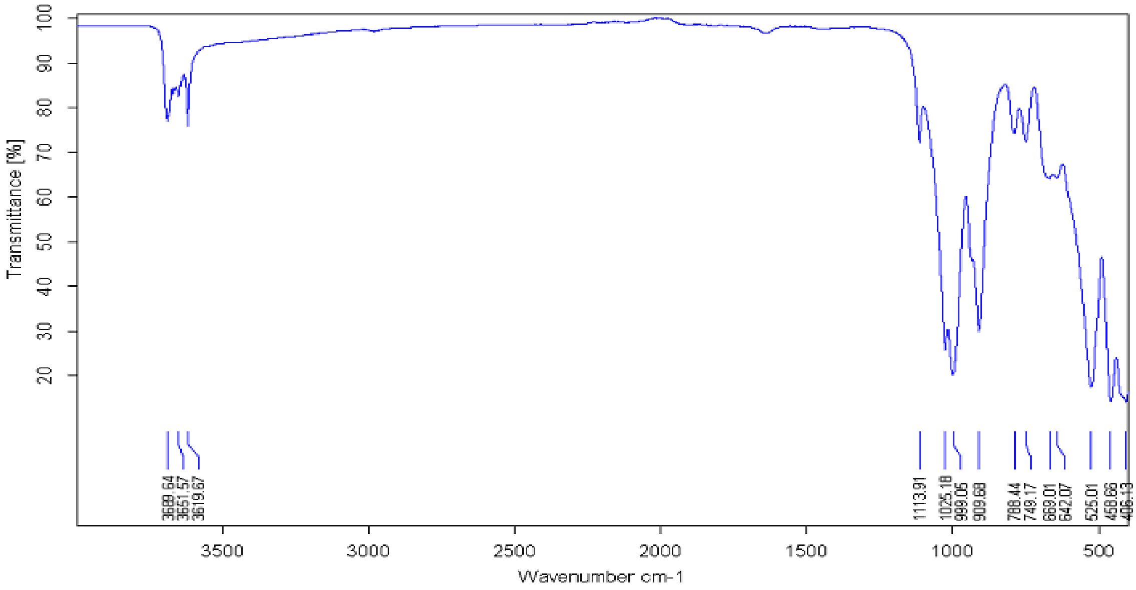

Fig. 2: FT-IR Spectrum of K-Clay

SEM/EDS:

The results of surface morphology and elemental composition of K-clay and K-S clay are shown in Fig. 3. Comparative analysis of the SEM micrographs showed the orientation of K-clay exhibited a predominant filmy particles stacked in layers. The microstructure of K-S showed variable cluster of flake-like particles. The EDS spectra reveals the presence of aluminum, silicon and oxygen as the predominant elements in K-clay (Fig. 4). Iron, potassium, calcium and titanium were present in trace amount as shown in the elemental composition. Folorunsho *et al.* (2014) reported oxygen, silicon and aluminum as the predominant element in three Nigerian kaolinite clays. Different signal intensities and weight (%) observed for the elements after modification with NaOH showed there was complete removal of Carbon in K-S and the weight of Oxygen increased from 48.85% to 54.62% (Table 2). Al-Al_2O_3 substantially increased from 13.36% in K-clay to 15.58% in K-S clay while Si-SiO_2 increased from 15.92 to 24.81% respectively. Sodium observed in K-S (0.75%) can be attributed to the interaction of NaOH with the clay surface. In a recent report (Heah *et al.*, 2013), the sodium content of a modified kaolinite clay was found to increase from 0.20 to 2.47%.

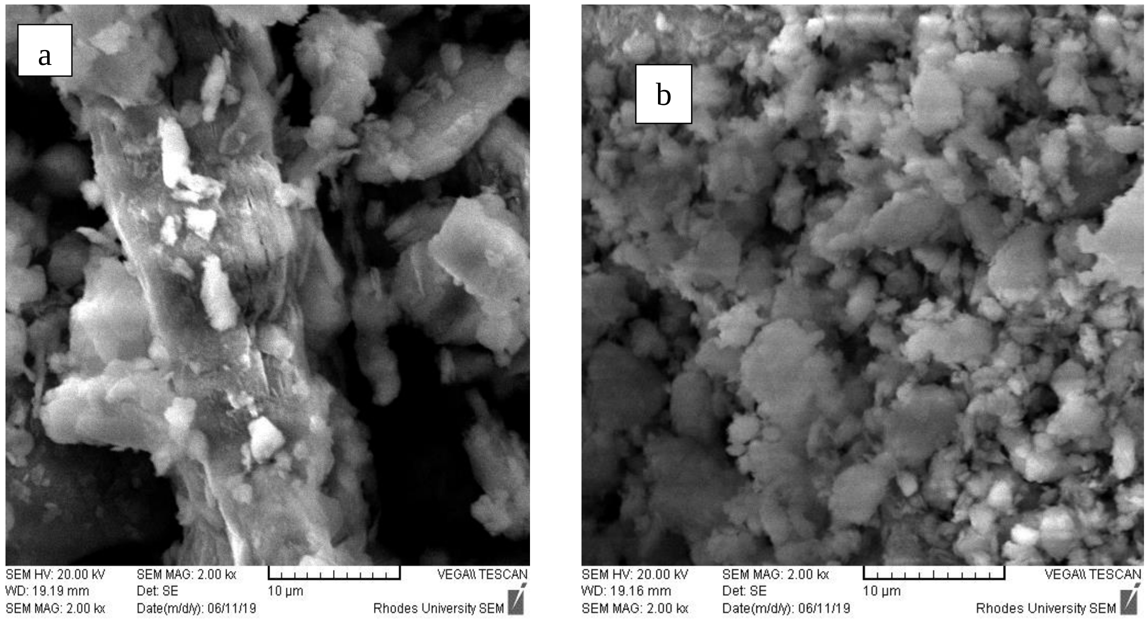

Fig. 3: SEM image of: (a) K-clay (b) K-S clay

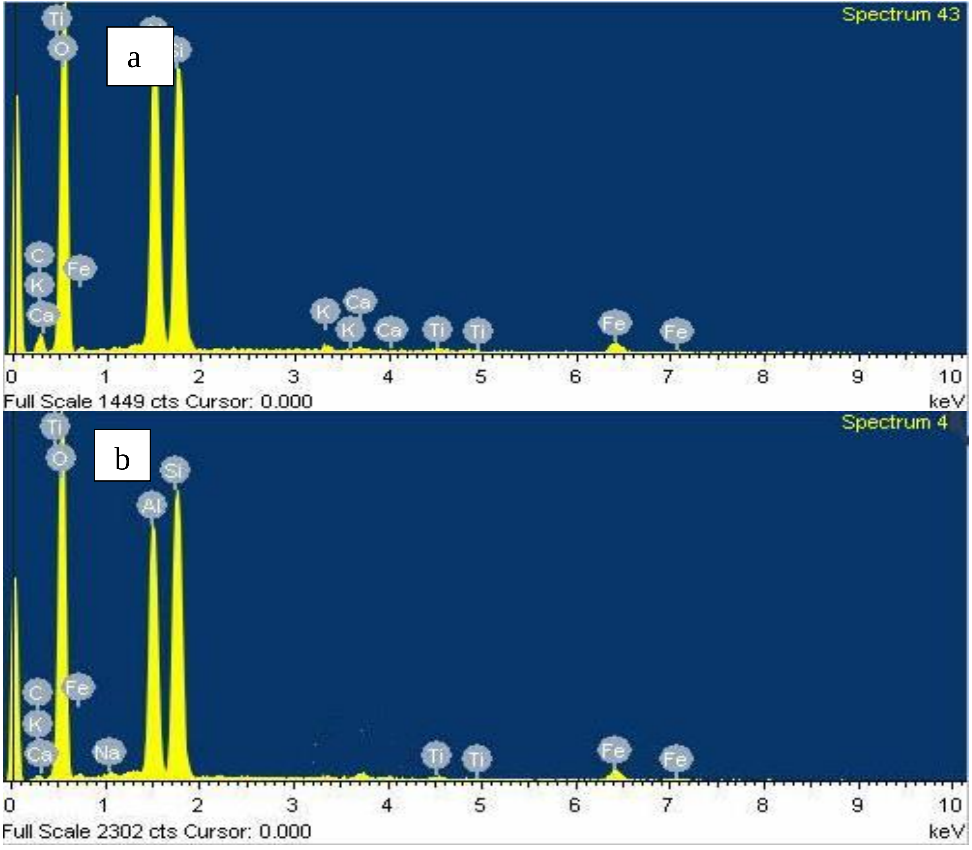

Fig. 4: EDX Spectra: (a) AK-clay (b) AK-S clay

Table 2: Elemental Composition of K-clay and K-S clay

Element	AK-clay Weight (%)	AK-S Weight (%)
C	6.51	-
O	48.85	54.92
Na	-	0.75
Al	13.36	15.58
Si	15.92	24.81
K	0.32	0.21
Ca	0.25	0.53
Ti	0.28	0.31
Fe	2.49	2.31
Total	87.98	99.42

Adsorption of Metal Ions from the Steel Effluent on K-S Clay

The initial concentrations of metal ions detected in the effluent were 309.0, 20.50, 40.40 and 10.90 mg/L for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+}ions respectively. From the results (Fig. 5 and Table 3), adsorption of Fe^{2+} from the effluent at pH of 3.0 on K-S clay in the first cycle recorded removal efficiency of 38.95% and 42.39% in the first 15 and 30 minutes respectively. Contact time of 60 to 240 minutes were characterized by low or no significant increase in adsorption to reach equilibrium capacity of 48.38% (37.36 mg/g) at 240 minutes. Uptake of Pb^{2+} ion was rapid in the first 15 minutes (16.10%, 0.83 mg/g) and then gradually increased from 30-150 minutes to 26.83% (1.38 mg/g) after which a near state of equilibrium was maintained till 240 minutes at which removal efficiency of 28.78% (1.48 mg/g) was achieved. Near state of equilibrium was attained in the first 15 minutes (5.94%, 0.63 mg/g) for the adsorption of Zn^{2+} ion. Above this contact time, little or stable increase was observed as the time progressed to 240 minutes where adsorption capacity of 1.55 mg/g (15.35%) was recorded. Adsorption of Cr^{6+} ion increased gradually from 15 minutes (20.18%, 0.55 mg/g to 240 minutes (37.6%, 1.03 mg/g).

Using the regenerated adsorbent for the second adsorption cycle resulted in removal efficiency of 38.56, 58.90, 28.07 and 27.94 % for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions respectively. The third adsorption cycle resulted in uptake of 53.47, 75.0, 62.60 and 63.27% for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions at contact time of 240 minutes. The amount adsorbed at the fourth adsorption cycle were 11.23, 0.37, 0.23 and 0.45 mg/g with final concentrations for Fe^{2+} (0.7 mg/L), Pb^{2+} (0.01 mg/L), Zn^{2+} (0.04 mg/L) and Cr^{6+} (0.01 mg/L) and total removal efficiency of 99.77, 99.95, 99.90 and 99.91 % respectively.

As the concentration of the metal ions decreased, the pH of the effluent increased from 3.0 to 4.8 at the fourth cycle without precipitation of the metal ions due to decrease in the concentration of the ions. Higher adsorption capacity for Fe^{2+} ion can be attributed to high number of its molecules available for interaction, which also increased its driving force to the binding sites than other metal ions (Jiang *et al*., 2009; Arivoli *et al*., 2013). This implies that the presence of Fe^{2+} ion at higher concentration hindered the rate of sorption of other metal ions. The adsorption capacity for each successive cycle follows the magnitude of the initial concentrations of the metal ions. Akpomie and Dawodu (2016) reported similar trend of higher adsorption capacity for Zn^{2+} ion over other metal ions ($Zn^{2+}> Cu^{2+}> Mn^{2+}> Cd^{2+}> Pb^{2+}> Ni^{2+}$) from an automobile effluent in sequence relating directly to the magnitude of their initial concentrations. In another report (Beh *et al*., 2012), adsorption of heavy metals from steel making wastewater on electric arc furnace slag in a fixed-bed column mode recorded decrease in concentrations of Fe^{2+}, Zn^{2+}, Mn^{2+} and Cu^{2+} ions from 23.3, 1.02, 1.56 and 0.83 mg/L to 0.08, 0.01, 0.03 and 0.07 mg/L respectively.

For each of the four adsorption cycles, the decreasing order of adsorption, based on amount adsorbed in mg/g, is $Fe^{2+}> Zn^{2+}> Pb^{2+}> Cr^{6+}$ ions. For all the metal ions, the amount adsorbed decreased with increase in adsorption cycle and the pH of the solution also increased with increase in adsorption cycle. Using Fe^{2+} for illustration, the amount adsorbed was 37.38 mg/g, 15.38 mg/g, 13.10 mg/g and 11.23 mg/g for the first, second, third and fourth adsorption cycles respectively and the pH measured were 3.0, 3.5, 4.2 and 4.8 respectively.

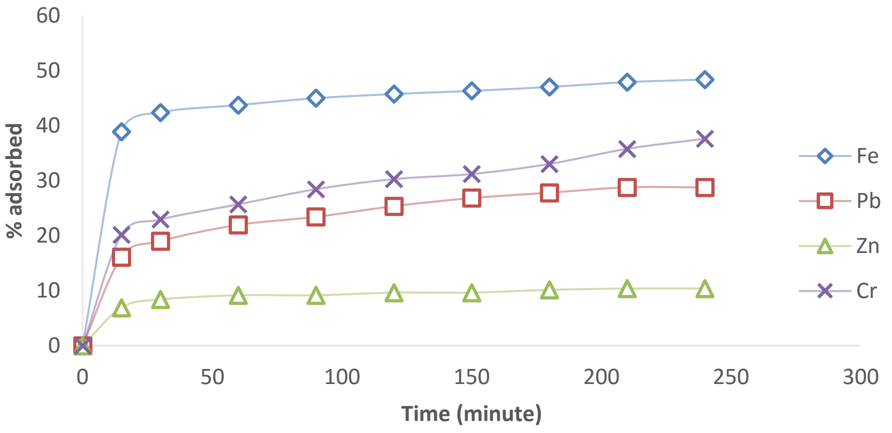

Fig. 5: First adsorption cycle for Fe^{2+}, Pb^{2+}, Zn^{2+} and Cr^{6+} ions from the effluent on K-S clay

Table 3: Adsorption cycles for steel processing effluents on regenerated AK-S clay

Metal ions		**Fe**	**Pb**	**Zn**	**Cr**
	Initial Con. C_i (mg/L)	309.0	20.50	40.40	10.90
First adsorption (pH 3.0)	Final conc. C_x (mg/L)	159.50	14.60	34.20	6.80
	% adsorbed	48.38	28.78	15.35	37.62
	Amount adsorbed (mg/g)	37.38	1.48	1.55	1.03
Second recycling (pH 3.5)	Final conc. C_x (mg/L)	98.0	6.0	24.60	4.90
	% adsorbed	38.56	58.90	28.07	27.94
	Amount adsorbed (mg/g)	15.38	2.15	2.40	0.48
Third cycling (pH 4.2)	Final conc. C_x (mg/L)	45.60	1.50	9.20	1.80
	% adsorbed	53.47	75.0	62.60	63.27
	Amount adsorbed (mg/g)	13.10	1.13	3.85	0.78
Fourth cycling (pH 4.8)	Final conc. C_x (mg/L)	0.70	0.01	0.04	0.01
	% adsorbed	98.48	99.33	99.57	99.44
	Amount adsorbed (mg/g)	11.23	0.37	0.23	0.45
Total % adsorbed		99.77	99.95	98.91	99.91

Physicochemical Characteristics and WQI/MPI of the Effluent before and after Adsorption on K-S Clay

Table 4 presents the physicochemical characteristics of the steel effluent before and after adsorption. The results of the physicochemical parameters of the raw effluent were pH 1.13 ± 0.003, EC 10203 ± 2.65 µS/cm and 40 ± 1.73, 1225 ± 3.0, 4.68 ±0.11, 119 ± 1.0, 121 ± 2.65, 1768 ± 4.36 and 367 ± 1.73 mg/L for TSS, TDS, DO, BOD, COD, chloride and sulphate ion respectively. With the exception of DO, all other parameters were critically above the recommended permissible limits (WHO, 2011; NESREA, 2011). The acidic nature, high degree of EC and chloride ions in the effluent can be attributed to wastewater streams generated from acid pickling for descaling the surface of the steel raw materials. High TDS value observed was due to the dissolution of metal dusts and other solid particles by the action of acid solution used during pickling and grinding process. COD was relatively higher than the BOD value; an indication that the effluent contains more of biodegradable resistant organic compounds (Ram *et al*., 2011). After successive adsorption cycles on K-S clay, the magnitude of the various parameters decreased to reasonable level acceptable for industrial discharge.

The values of WQI and MPI obtained from the physicochemical parameters and metal ion concentrations before adsorption were 1087.19 and 17929.25 respectively. These values which are higher than the critical pollution level confirm that all the parameters were at toxic level when compared with water quality standards of WHO (WHO, 2011;Tyagi *et al*., 2013). After successive adsorption on K-S clay, the WQI reduced to 187.94, while the MPI reduced to 86.35. The value of WQI was above the critical pollution level while that of MPI fall in the range of very poor water quality range of 76-100 (Table 1). The overall index (WQI and MPI) after treatment showed the adsorption process successfully removed the metal ions and other contaminants in the wastewater to a level acceptable for industrial discharge but of poor quality for drinking based on water quality rating.

Table 4: Physicochemical properties of the effluent before and after adsorption

Parameters	pH	Cond. (µS/cm)	TSS (mg/L)	TDS (mg/L)	DO (mg/L)	BOD (mg/L)	COD (mg/L)	Chloride (mg/L)	Sulphate (mg/L)
Before adsorption	1.13 ±0.03	10203 ±2.65	40 ± 1.73	1225 ± 3.0	4.68 ± 0.11	119 ± 1.0	121 ± 2.65	1768 ± 4.36	367 ± 1.73
After adsorption	5.62 ± 0.05	201± 2.65	6.0 ± 0.87	22 ± 1.5	6.87 ± 0.04	13± 1.73	25 ±1.73	195 ±2.65	92 ± 2.65
WHO Standard Limits	**6.5-8.5**	**300**	**500**	**500**	**5.0**	**5**	**10**	**250**	**250**
NESREA Standard Limits	**6.0-9.0**	**-**	**500**	**500**	**4.0**	**30**	**60**	**350**	**500**

CONCLUSION

The results of mineralogical composition of the purified 63 µm fraction of the natural clay minerals show that the Argungu clay (K-clay) is kaolin with favourable properties such as high alumina and silica and low iron content. The results of Water Quality and Metal Pollution Indices (WQI/MPI) revealed that the physicochemical parameters of the steel processing effluent were above the critical pollution index. Application of K-S clay for the remediation process in successive adsorption cycles, resulted in reduction of the heavy metal ions present in the effluent and reduction of other physicochemical parameters to a level that meet the requirement for industrial discharge. Regeneration and reuse of the spent adsorbents for the successive adsorption cycle without reducing the adsorption capacities indicates the efficiency and economic viability of the studied clay adsorbent for remediation of steel processing effluents.

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