Comparative Carbon Synthesis of Peat Using $ZnCl_2$and $H_3PO_4$for Heavy Metal Adsorption in Oilfield Produced Water

ABSTRACT

Oilfield Produced Water is one of the amplest wastes resulting from oil and gas operations and it's of great industrial concern due to its quantity, concentration, and cost of treatment; thus, it needs cheaper and more available options. Peat being an option is a renewable brown deposit resembling soil, formed as a result of an accumulation of organic matter, also known to have a rich carbon content. This research work aims to comparatively synthesize peat soil with $ZnCl_2$ and H_3PO_4, carbonize, characterize, and determine the efficiency of heavy metal adsorption in Oilfield Produced Water. The peat sampleswere collected from Warri City commonly referred to as Oil City in southern Nigeria andwere impregnated with $ZnCl_2$ (PAC-ZC); H_3PO_4 (PAC-HP); $ZnCl_2$ and H_3PO_4 at a ratio of 1:1 (PAC-ZC+HP) and with De-ionized water as control (PAC-D). After activation, peat was carbonized at 400^oC for 1 hour. Fourier-Transform Infrared Spectroscopy analysis showed all five samples have a strong silicate ion peak between 998.9 - $1028.7cm^{-1}$, the presence of Vincy C-H group at $909.5cm^{-1}$, broad shaped polar O-H bond between 369.5 – $3623.0cm^{-1}$ and an adsorption peak between 2929.7 – $2012.8cm^{-1}$ which disappeared after activation and carbonization. Scanning Electron Microscopy micrograph shows a surface enhancement after activation and carbonization. The heavy metals (Pb, Cu, Ni, Zn & Fe) level in the Oilfield Produced Water was analyzed before and after treatment with Peat Activated Carbon using Atomic Absorption Spectrometry. Four dosages (1,2,3, and 4g) of each Peat Activated Carbon were used to treat 100ml of Oilfield Produced Water. PAC-ZC and PAC-ZC+HP showed 100% efficiency in the removal of turbidity, Pb, Cu, Ni, and Fe. However, the overall efficiency trend of the adsorption capacity of the Peat Activated Carbon was PAC-ZC > PAC-ZC+HP > PAC-HP > PAC-D. With the experimental result, PAC-ZC and PAC-ZC+HP can be used as treatment options for Oilfield Produced Water.

***Keywords**: Activated Carbon; Heavy Metals; Oilfield Produced Water; Peat;Peat Soil; Waste Water Treatment.*

INTRODUCTION

Water is one of the most abundant resources known to man but yet a little scarce in terms of usage. Water is said to cover about 71% of the world's land mass [1], covering a total of 1.386 billion km³. Water has a variety of characteristics, ranging from its chemical to its physical properties [2] but amongst water's numerous characteristics, its ability to be a universal solvent, makes the water quite unique but can also be regarded as a blessing and a curse. Water easily dissolves almost anything, ranging from gases to heavy metals (referene). Water can naturally dissolve gases from the atmosphere [3] and heavy metals, by just flowing across rocks. Formation water is an example of water that naturally accumulates high concentrations of heavy metals and gases (reference).

Formation water is water confined in the pores of rocks during their formation before the percolation of crude oil and gas (reference). The chemistry of this water largely depends on the characteristics of the; housing rock, the crude oil and gas trap in the formation, and the source of the formation water. This porous rock housing formation water, crude oil, and gas is called a petroleum reservoir. The petroleum reservoir is drilled through during oil and gas production, to extract the crude oil, gas, and formation water(reduce this to one sentence and cite the source of this information). In the course of production, formation water is subsequently called produced water. According to Reference [4,5] produced water is said to be an average of three times the quantity of crude oil and gas in the well, with this ratio most likely to increase as the well gets older.

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In 1987, ~~Reference [6],~~It was established a fact that produced water was not just water containing oil (ref). A produced water sample contained up to 48 parts per million (ppm) of petroleum, which was understandable because water had been in ~~contain~~ contactwith oil for millions of years in the reservoir[6,7,8]. More surprisingly, was it intolerable concentration of metals such as lead, copper, iron, nickel, zinc, cadmium, chromium, beryllium, and barium; trace level radioactive elements like radium226 and radium228; dissolved gases like hydrogen sulphide and carbon dioxide at notable concentrations; microorganisms and polycyclic aromatic hydrocarbons[9].

Due to the high concentration of contaminants in produced water and with special recalls to its metal concentration, it's usually difficult to handle produced water. However, Oilfield Produced Water (OPW) can be discharged into seawater, where they are diluted. Thereby posing slimily no serious danger to aquatic animals. On the other hand, in situations where the production wells are cited in the land, creeks, and shallow waters, OPW disposal poses a serious concern to the environment noting their excessive concentration of salts, organics, and especially metals.

Heavy metals are known to alter the physiology of humans and other lower biologically active systems when they rise to levels that exceed tolerance [10]. Heavy metals which appear to be non-biodegradable causes a wide range of disorder and disease in living organism due to their tendency to accumulate in living organisms (ref).

The fact that heavy metals pose such grave effects on living organism and their ecosystem has led to the discovery of methods effective in the removal of heavy metals from waters with obnoxious levels of pollutants. These include ion exchange, reverse osmosis, membrane filtration, chemical precipitation, and adsorption (ref). These methods have proven to be successful in their functions but have drawbacks that are worthy of note; thus, they have a high cost of operation and residual disposal issues, which in some cases generate new waste that also needs treatment [11]. The high capital-intensive operation cost and residual disposal issues have become discouraging and a source of concern for small start-up industries. Hence the a(correct grammar) need for treatment methods that are low-cost and low-capital intensive. However, there are reports on the availability and development of low-cost adsorptive materials also known as activated carbon produced from readily available materials [12].

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Activated carbon is a material with high carbonaceous content with high surface area, microporous character, and a surface with a distinctive chemical nature, which have made them possible adsorbents for the removal of heavy metals from wastewater obtained from industrial processes[13]. Activated carbon is manufactured from a wide variety of materials such as coal, wood, hazelnut shelland coconut shell, ~~and~~ ~~recently peat~~(remove pet) (ref). Agricultural by-products such as apricot stones, grape seeds, shells of almonds, nuts, peach stones, and extracted oil palm fibers are not left out as they have been found to produce a fairly good activated carbon (ref).

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Peat is a renewable resource, which before now has been ignored, perhaps because of its lack of popularity [14]. Peat is a brown deposit resembling soil, formed as a result of an accumulation of organic matter or vegetation that has partially decayed. Although, nowadays, peat has been mainly used as a heating energy resource instead of other purposes. On the other hand, countries like Finland, have started the usage of peat to produce activated carbon, which has gained some interest among researchers and companies in order to find new applications for the peat [15].

Industrial wastewater such as Oilfield Produced Water is said to be the highest liquid waste in the oil and gas industry today, also contributing to the presence of Persistent Organic Pollutants (POPs), Polycyclic Aromatic Hydrocarbons (PAHs), and excessive and extremely high presence of heavy metal ref. These pollutants have been directly linked to being the leading cause of poisoning, biomagnification, and bioaccumulation in animals, especially in aquatic environments ref. They also adversely affect soil and plants, which impairs their growth, leading to a shortage of food supply, particularly when disposed of on land without adequate treatment ref. Oilfield Produced Water should undergo specific treatment before its discharge into a water body. Adsorption treatment using good carbon sources can be an effective method of treatment [16]. The success of Peat for adsorption would be a plus to the oil and gas technology as produced water treatment technology equipment like; American Petroleum Institute (API) Separators, Hydroclones and reverse osmosis are exceptionally expensive. On the other hand, Peat is in abundance in Ifie community and beyond in the western Niger Delta. Nigeria without any particular use by the indigenes and can be used for this adsorption experiment. Peat is usually been referred to as barren land by some locals in the community. The materials used as precursors have different capabilities to adsorb different types and speciation of metal ions due to their high adsorption capabilities and the functional groups on the activated carbon surface [17] and have a prospect of being very affordable. This research work aims to comparatively (How) synthesize a carbonized peat with $ZnCl_2$and H_3PO_4, characterize and determine the efficiency, of the adsorption of heavy metals from OPW.

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2. MATERIALS AND METHODS

Peat sampleswere collected fromWarri City (latitudinal and longitudinal coordinates missing) commonly referred to as Oil City in southern Nigeria using a soil auger at a depth of 20cm and transferred to a polythene bag. OPW was sampled from the sampling valve at the wellhead terminal of an oil and gas production company in Delta State, Nigeria. This was done using a glass sample bottle (explain further the type of the bottle). After sampling nitric acid was added to the OPW sample to keep the metals in solution which will prevent precipitation, metal adsorption to the surface of the glass wall, and degradation by microorganisms.

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How was the sample transported to the laboratory?

How much of the samples were collected?

What sample parameters were taken and recorded in the field?

List of equipment and reagents used missing.

Season of sampling missing.

2.1 Pre-treatment

The collected peats were washed with deionized water to eradicate possible contaminants (mud, sand, and dirt) present in the sample. The washed sample material was dried in an oven at 105^{o}C for 2hrs and then crushed using a mortar and pestle to reduce the size of the dried peat (ref) or new method?.

The crushed and dried peat was acid-washed in a fume cupboard with 1M of Hydrochloric acid for the dissolution of heavy metals and mineral content in the peat [18].

How much of 1M HCl used?

2.2 Carbonization

The four samples except the raw peat (RP) were individually placed in ceramic crucibles and carbonized. The samples were placed in a furnace to carbonize (check tense) at 400^{o}C for one hour. After the one-hour mark, the sample was left to sit(not scientific) for an extra hour before opening the furnace. The sample was removed from the furnace using a crucible tong and placed in a desiccator to cool.(ref)

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2.3 Chemical Activation

200g of crushed acid-washed peat was shared into four equal parts (50g each) and labeled PAC-ZC, PAC-HP, PAC-ZC+HP, and PAC-D. The four samples were placed into four different 1000ml beakers. Sample A was impregnated with 0.1 M $ZnCl_2$ solution, Sample B was also impregnated with a 0.1 M H_3PO_4 solution, sample C was impregnated with 0.1 M solution of $ZnCl_2$ and 0.1 M H_3PO_4 solution at an impregnation ratio of 1:1 and Sample D which acted as the control was soaked with deionized water. All samples were left to sit for 24 hours.

After 24 hours, the activation chemicals were washed off using deionized water till they reached a pH of 7. Afterward, the samples were allowed to dry in an oven at 105^{o}C for 1hour.

2.4Peat Activated Carbon Characterization

The infrared (IR) spectrum of the PAC was determined using an Agilent Cary 630 FT-IR Model (country of Origin), operating in the 4000 – 400cm^{-}1 range. PAC sample was grounded alongside an IR spectroscopy grade KBr crystals to form a thin film, which was then placed in the sample cup holder for analysis ref.

The pore structure, surface morphology, and elemental composition (SEM-EDX) of the PAC sample were determined using a Phenom ProX 800-07334 SEM Desktop Model (country of origin)

The Peat Activated Carbon sample was further characterized to determine its specific surface area, pore diameter, and pore volume. This was analyzed using N_2 adsorption at a temperature of -196^{o}C with surface area and pore size analyzer (Quantachrome Nova 4000E BET Machine). T-Plot micropore volume was used to compute the micropore volume. Barrett-Joyner-Halenda (BJH) mode was used to determine the pore size distribution.

The heavy metals; Pb, Fe, Zn, Cu, and Ni concentrations of the Oilfield Produced Water (OPW) were determined using a Shimadzu AA-6800 Atomic Absorption Spectrophotometer before and after treatment with PAC. A turbidity meter was used to determine the cloudiness of the OPW.

Include the country of origin to all machines used in analysis

2.5Efficiency of Peat Activated Carbon

100 ml of the oilfield Produced water was poured into ~~seventeen (~~(seventeen (17) different 1000 ml conical flasks. A1 wasn't treated with activated carbon, as it acted as a control, C1, C2, C3, and C4, were treated with a carbonized peat at four different doses, 1g, 2g, 3g, and 4g respectively; H1, H2, H3, and H4, were treated with H_3PO_4 activated carbon at four different doses; 1g, 2g, 3g, and 4g respectively; Z1, Z2, Z3, and Z4, were treated with $ZnCl_2$ activated carbon at four different doses; 1g, 2g, 3g, and 4g respectively; HZ1, HZ2, HZ3, and HZ4, were treated with H_3PO_4 and $ZnCl_2$ activated carbon at four different doses; 1g, 2g, 3g, and 4g respectively.

These sixteen samples were kept in an orbital shaker in different batches to shake at a speed of 200rpm at ambient temperature (32^{o}C) and for a period of 30mins (was this the optimum contact time?) to ensure proper mixing. After this, the suspension from the activated carbon was filtered using a Whatman filter paper.

The concentration of the heavy metal in the filtrate was determined using an Atomic Absorption Spectrophotometer. (Type)

The formula for Efficiency is thus;

Efficiency $= \frac{CO - C1}{CO} \times 100$ was used to determine the optimal activated peat dosage (ref).

Where C_O is the initial concentration of heavy metal

Where C_1 is the final concentration of heavy metal.

3. RESULT AND DISCUSSION

Peat Activated Carbon (PAC) was produced and successfully activated with $ZnCl_2$ (PAC-ZC), H_3PO_4 (PAC-HP), and with a 1:1 ratio of $ZnCl_2$ and H_3PO_4 Acid (PAC-ZC+HP).

These Peat Activated Carbons (PACs) after activation were characterized using the Fourier-Transform Infrared Spectroscopy (FTIR) to identify the active compounds present in the PAC, Scanning Electron Microscopy (SEM) to determine the surface morphology of the PAC, Energy Dispersed X-Ray (EDX) to determine the elemental content of the PAC, and BET (Brunauer, Emmett, and Teller) and the BJH (Barrett, Joyner, and Halwnda) (ref)methods were usedto determine the surface area and adsorption capacity of the PAC. The specific surface area of the various adsorbents was calculated using nitrogen adsorption/desorption isotherms at 77K.The characterized Peat Activated Carbons (PAC-D, PAC-ZC, PAC-HP & PAC-ZC+HP) were successfully used to treat an oilfield produced water at four different dosages (1, 2, 3, & 4g).

3.1 Characterization of Peat Activated Carbon

The result from the characterization of the Raw Peat (RP), Carbonized, and Activation of Peat is shown below.

(i) Fourier-Transform Infrared Spectroscopy Analysis (FTIR)

The presence of functional groups at the surface of an activated carbon (AC) is one of the factors that determines the adsorptive capacities of the activated carbon to attract metal ions to its surface [17]. The FTIR spectrum as seen in Figure 1, showed that all five samples have a strong and sharp peak between 998.9 to 1028.7cm^{-1}, indicating the presence of silicate ions

Si-O-Si. It was also observed that the peak significantly increased from 998.9cm-1 in RP to 1028.7cm^{-1} in PAC-D, PAC-HP, and PAC-ZC-HP. Thisagrees with ~~Reference~~ [19] that the silica structures in PAC change with carbonization (temperature change). However, PAC-ZC showed no change at the silicate ion spectrum peak. The second most noticeable spectrum peak 909.5cm^{-1} is Vinyl C-H group ($-CH=CH_2$), which was observed in all five samples; RP, PAC-D, PAC-ZC, PAC-HP, PAC-ZC+HP with peak intensities of 72.614, 67.316, 49.068, 67.700 and 73.844 respectively. A change in peak intensity usually suggests an increase or decrease in the amount per unit volume of the functional group associated with the molecular bond [20].

The weak broad absorption bands between 3697.5 – 3623.0 cm^{-1} in all five samples are attributed to the polar O–H bond. The broad shape of the adsorption band results from the hydrogen bonding of the OH^{-} bond of the alcohol group. The adsorption peaks between 3488.8 – 2929.7 cm^{-1} correspond to O–H stretching vibration of the adsorbed water on the surface of RP and PAC-ZC+HP, which shows signs to have been affected by carbonization and the chemical treatment of $ZnCl_2$ and H_3PO_4, thereby causing them to disappear in the corresponding adsorbents. The disappearance of the absorption peaks between 2929.7 - 2012.8 cm^{-1} in the PAC-D, PAC-ZC, and PAC-HP spectra can be attributed to the loss of cellulosic content [21]. Furthermore, Reference [22] also explained that after carbonization and activation, the loss of organic matter band (~1750 cm^{-1} and above) of the polar functional groups like; alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides are as a result of their low thermal stability.

(ii) Surface Morphology

Fig. 2 shows the SEM image of the morphological studies of raw, carbonized, and chemically activated peat. The micrographs show the rough surface of the prepared raw adsorbent which was enhanced by carbonization and chemical activation. These irregular channels on the surface of the adsorbent are for the adsorption of pollutants [23]. RP seems to have a smiley smoother surface before the carbonization and chemical treatment. Packs of a layered structure with more flat surfaces and parallel sheaths were more pronounced on PAC-HP followed by PAC-ZC and then PAC-ZC+HP. The morphology of each layer became more obvious as the magnification was increased to 800x. However, the pore structure was not clearly defined. Probably because a bit of tar remained on the surface of the activated peat and perhaps clogged the micropores [24].

(iii) Chemical Composition

The chemical elements were identified by using EDX based on the spot analysis. RP, PAC-D, PAC-ZC, PAC-HP, and PAC-ZC+HP were all analyzed using two randomly selected spots because peat naturally contains two distinct materials, which are peat moss (*Sphagnum*) and peat soil. This was significantly highlighted in the chemical composition of RP (Raw peat). In RP, spot 1 showed a ratio of almost 1:4 for silica atoms (16.98%) and oxygen atoms (60.73%), indicating a general SiO_4 tetrahedron structure. The additional presence of Aluminum (7.04%), further suggests the presence of a more complex structure like Kaolinite ($Al_2O_3\ 2SiO_2 \cdot 2H_2O$), uncharged dioctahedral layers with a single silica tetrahedral sheet, and a single alumina octahedral sheet in each layer [25], with trace concentration of Nitrogen (8.82%) and Potassium (5.41%) suggesting a mildly healthy peat soil. Spot 2 showed a higher concentration of carbon (31.68%) when compared to spot 1. The carbon concentration obviously indicates the presence of peat moss.Both spots 1 and 2 showed a noticeable introduction of Zinc (37.69% and 5.93%) and Chlorine (25.03% and 1.80%) to PAC-ZC after the carbonization and chemical activation with $ZnCl_2$ when compared to PAC-D (control) which had no observed concentration of Zinc and Chlorine. This is because the control was carbonized and activated with deionized water. Similarly in PAC-HP, when compared to PAC-D, Phosphorus was introduced at spots 1&2 (2.02% and 2.13%) and increase in Oxygen from 47.19% and 37% to 70.36% and 66.90% in spots 1&2 respectively. PAC-ZC+HP , a hybrid chemical activation of $ZnCl_2$ and H_3PO_4 acid, also shows an increase in Zn, Cl, P, and O. This increase indicates a change in the activated carbon surface morphology, being coated with the chemical activating agents used in this work. At PAC-D the Silica atomic concentration percentage was the highest and was seen to increase by carbonization from 16.98% and 9.19% to 29.54% and 16.61% in spots 1&2 respectively. A similar trend was also observed by Reference [19].

Improve on your citation of the explanations of the findings.

(iv) Surface Property

The BET specific surface area of the adsorbent is an important and useful factor in determining the adsorption capacity of the adsorbent. This is due to its influence on the reaction or carbonization process, where there is a possibility of opening the restricted pores [26]. Nitrogen gas is commonly employed due to its high purity and strong interaction with most substances. The adsorptive capacity of activated carbon is related to its specific surface area (S_{BET}), pore volume (V_{MICRO}), and pore size distribution (PD). Generally, as the surface area of the activated carbon increases, its adsorptive capacity will also increase [27,28]. These surface areas are generated gradually during the activation processes.

From BET analysis, PAC-D has the highest values of specific surface area value of 706.906 (m^2/g) and pore volume of 0.425 (cm^3/g), while PAC-ZC has the least specific surface area and pore volume values of 109.474 (m^2/g) and 0.061 (cm^3/g) respectively. Specific surface area and pore volume values 353.749 (m^2/g) and 0.196 (cm^3/g) were recorded for PAC-ZC+HP while PAC-HP had values of 185.979 (m^2/g) and 0.104 (cm^3/g) respectively. The adsorbents are seen to have a mesoporous structure with a pore diameter in the range of 2.118-2.133 (nm).

Label these diagrams correctly e.g. FTIR spectroscopy of PEAT before adsorption and not as abcd

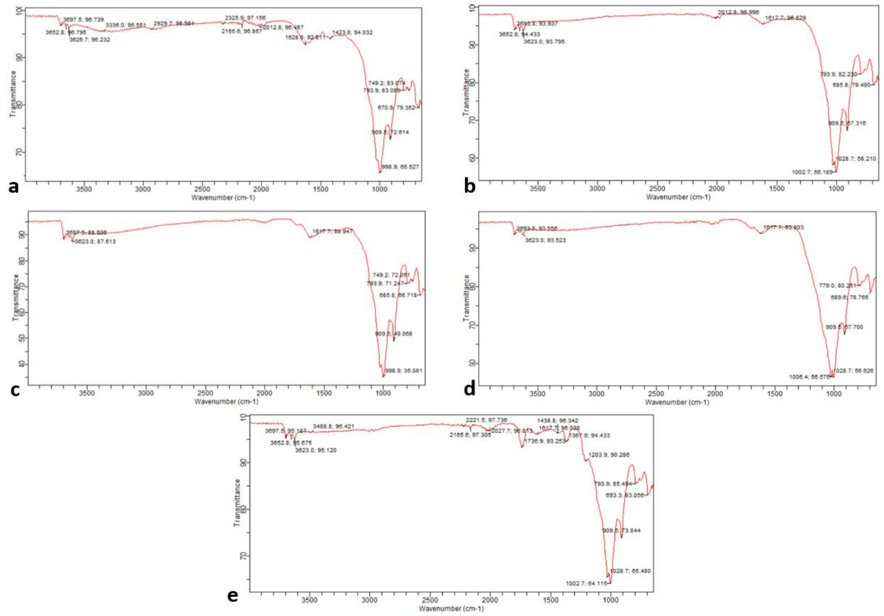

Fig. 1. FTIR Spectra of Raw, Carbonized, and Chemically Activated Peat:*(a) RP: Raw Peat; (b) PAC-D: Carbonized; (c) PAC-ZC: Activated with $ZnCl_2$; (d) PAC-HP: Activated with H_3PO_4; (e) PAC-ZC+HP: Activated with $ZnCl_2$ & H_3PO*

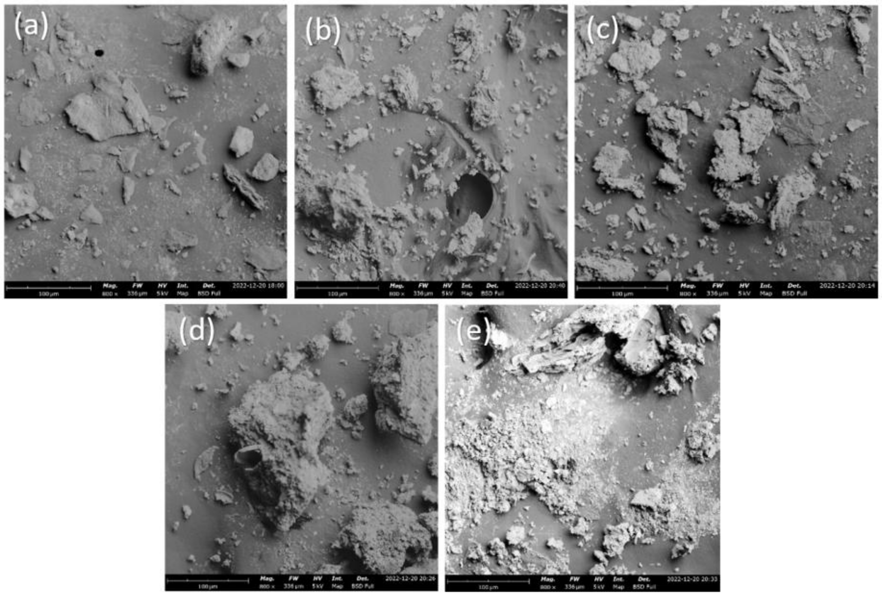

Fig. 2. SEM images of Raw, Carbonized, and Chemically activated Peat samples at 800x magnifications.*(a)RP: Raw Peat; (b)PAC-D: Carbonized; (c)PAC-ZC: Activated with* $ZnCl_2$*; (d)PAC-HP: Activated with* H_3PO_4*; (e)PAC-ZC+HP: Activated with* $ZnCl_2$ *&* H_3PO_4

Table 1: Chemical composition of Raw, Carbonized, and Chemically Activated Peat in terms of weight and atomic %

	RP				**PAC-D**				**PAC-ZC**				**PAC-HP**				**PAC-ZC+HP**			
	Spot 1		**Spot 2**		**Spot 1**		**Spot 2**		**Spot 1**		**Spot 2**		**Spot 1**		**Spot 2**		**Spot 1**		**Spot 2**	
Element	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**	**A (%)**	**W (%)**
O	60.73	48.93	41.50	31.45	47.19	31.85	37.00	21.85	17.50	5.89	43.05	25.35	70.36	56.46	66.70	56.82	32.09	18.41	31.01	14.56
Si	16.98	24.02	9.19	12.22	29.54	35.01	16.61	17.22	2.12	1.26	22.07	22.82	16.41	23.12	12.27	18.34	27.32	27.50	20.75	17.11
C	1.02	0.62	31.68	18.03	1.09	0.55	0	0			2.89	1.28	1.25	0.75	1.34	0.85			2.21	0.78
Al	7.04	9.56	0	0	16.55	18.83	9.98	9.94	2.26	1.28	11.66	11.58	9.10	12.31	7.44	10.69	18.16	17.57	12.74	10.09
K	5.41	10.64	5.96	11.03	0	0	5.97	8.61	0	0	5.53	7.96	0	0	0	0	2.04	2.86	0	0
N	8.82	6.22	0	0	0	0	13.18	6.81	0	0	0	0	0	0	9.12	6.80	0	0	0	0
Zn	0	0	0	0	0	0	0	0	37.69	51.87	5.93	14.26	0	0	0	0	3.85	9.01	14.17	27.18
Cl	0	0	0	0	0	0	0	0	25.03	18.68	1.80	2.35	0	0	0	0	3.65	4.63	3.47	3.61
P	0	0	0	0	0	0	0	0	0	0	0	0	2.20	3.42	2.13	3.51	6.12	6.79	1.15	1.04
Others	0	0	11.68	27.26	5.1	12.36	17.26	35.57	14.88	19.92	6.60	13.57	0.69	3.95	1.01	2.99	6.42	12.26	14.50	25.58

W: Weight Concentration; A: Atomic Concentration

Table 1 shows the elemental composition in terms of atomic % and weight % for all the peat samples. The chemical elements were identified by using EDX based on the spot analysis. RP, PAC-D, PAC-ZC, PAC-HP, and PAC-ZC+HP were all analyzed using randomly selected spots because peat naturally contains two distinct materials, which are peat moss (Sphagnum) and peat soil. RP: Raw Peat; PAC-D: Carbonized; PAC-ZC: Activated with $ZnCl_2$*; PAC-HP: Activated with* H_3PO_4*; and PAC-ZC+HP: Activated with* $ZnCl_2$ *&* H_3PO_4*.*

Table 2: The Surface Property of the Carbonized and Chemically Activated Peat.

AC Sample	**S_{BET} (m^2/g)**	**V_{MICRO} (cm^3/g)**	**PD (nm)**
PAC-D	706.906	0.425	2.118
PAC-ZC	109.474	0.061	2.133
PAC-HP	185.979	0.104	2.131
PAC-ZC+HP	353.749	0.196	2.123

Table 2 shows the BET Surface Area and Pore Sizes of Peat Activated Carbon. **S_{BET}***: BET Surface Area;* **V_{MICRO}***: Pore Volume;* **PD***: Pore Size Distribution. PAC-D had the highest BET Surface area and Pore volume of 706.906m^2/g and 0.425cm^3/g, while PAC-ZC had the lowest BET Surface Area and Pore volume of 109.474 m^2/g and 0.061 cm^3/g. PAC-HP and PAC-ZC+HP had their BET Surface Area and Pore volume as 185.979 m^2/g, 0.104 cm^3/g, and 353.749 m^2/g, 0.196 cm^3/g respectively. PAC-D: Carbonized; PAC-ZC: Activated with $ZnCl_2$; PAC-HP: Activated with H_3PO_4; and PAC-ZC+HP: Activated with $ZnCl_2$ & H_3PO_4*

3.2. Efficiency of Activated Carbon in Heavy Metal Removal

Fig. 3. shows the efficiency of activated carbon (AC) in the adsorption of heavy metals from produced water using different treatment dosages. The heavy metals of study are Pb, Cu, Ni, Zn, and Fe; the adsorption of colloidal particles was also examined as turbidity. The effectiveness of an adsorptivematerial is largely determined by the material's availability and accessibility to the pores of the material [29]. Four activated carbon dosages were used, 1g, 2g 3g, and 4g; under fixed conditions, which were; a neutral pH of 7, contact time of 30 mins, agitation speed of 200 rpm, and an ambient temperature of 32°C. (were these conditions optimized) After which, mixtures were filtered out and analyzed for their metal ion concentrations using Atomic Absorption Spectrophotometer.

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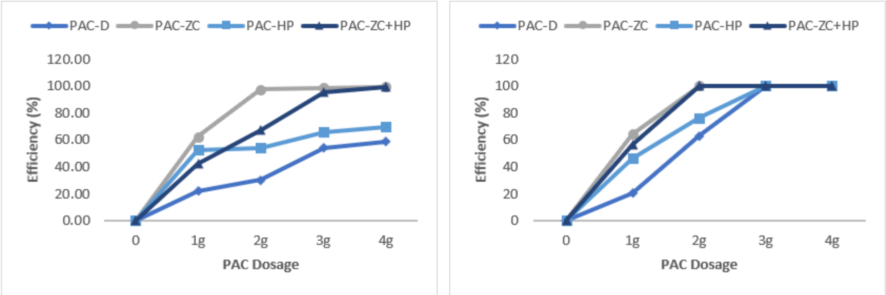
For turbidity, PAC-ZC and PAC-ZC+HP had the highest ratio difference in adsorption, with PAC-ZC reaching about 97%, 98%, and 99% in 2g, 3g, and 4g respectively and PAC-ZC+HP reaching 95% at 3g and 99% at 4g. However, PAC-D and PAC-HP reached an efficiency ratio of 58% and 69% at 4g respectively.

In the removal of Pb, all four adsorbents reached 100% at 3g but PAC-ZC and PAC-ZC+HP showed a superior adsorption ability by reaching 100% at a lower dosage of 2g. This shows $ZnCl_2$ activated carbon is a good adsorbent for Pb, which agrees with [30,31,32].

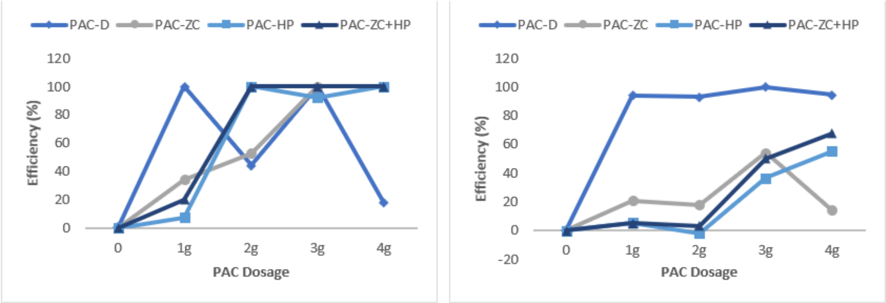
The adsorption capacity of Cu increased from 44 to 100%, 33.7 to 100%, 6.97 to 100%, and 19 to 100% at PAC-D, PAC-ZC, PAC-HP, and PACZC+HP respectively. This trend was anticipated because an increase in dose is an increase in available surface area (Archarya 2009), thus more Cu ions attach to the adsorbent surface [33].

Ni particle adsorption was highest at PAC-D reaching 100% at 3g but dropped at 4g to 94%. This could imply that PAC-D dosage was at equilibrium at 3g and experience a slight desorption.

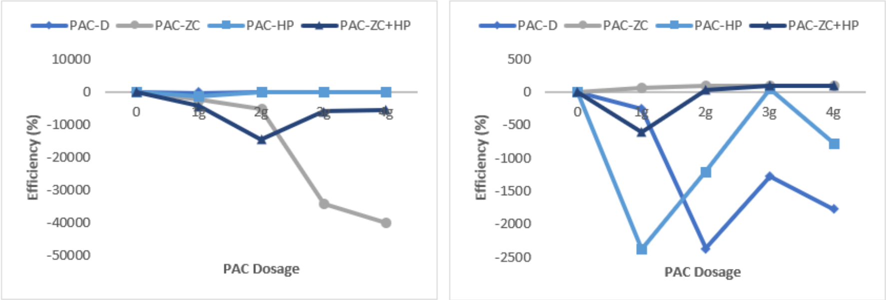
Zn and Fe had no adsorption but instead experienced desorption, likely from the activated carbon which was a result of the overlapping of adsorption sites due to overcrowding of adsorbent particles especially with PAC-ZC and PAC-ZC+HP; which were impregnated with $ZnCl_2$ during activation.



(a) Turbidity (b) Concentration of Lead (Pb)



(c) Concentration of Copper (Cu) (d) Concentration of Nickel (Ni)



(e) Concentration of Zinc (Zn) (f) Concentration of Iron (Fe)

Fig.3. Efficiency of Activated carbon (AC) in the adsorption of Heavy Metals from produced water at different treatment dosages.

4. CONCLUSION

Based on this research, PAC had a relatively good BET surface area. The average pore diameters obtained for all the adsorbents are larger than 2.1nm and this reflects their mesoporous nature. The SEM analyses of PAC-ZC, PAC-HP, and PAC-ZC+HP proved that a significant number of pores were developed during the activation process when compared to the Raw (RP)and Carbonized Peat (PAC-D). The FTIR analyses revealed the presence of different functional groups on the surfaces of the Raw, Carbonized, and Activated carbon. The removal efficiency of the prepared activated carbons were better than the carbonized peat (PAC-D). An increase in dosage of activated carbon in the adsorption of (Pb, Cu, and Ni) increased the adsorption uptakes of the activated adsorbent. The time (30 mins), shaking (200rpm), pH (7), and temperature (32^{o}C) were constant (Why). It was observed that the adsorption of all the cations onto the Peat activated carbon followed Type I isotherm for Turbidity, Pb, Cu, and Ni. The trend of adsorption capacity of the Peat activated carbon followed the order of PAC-ZC > PAC-ZC+HP > PAC-HP > PAC-D for Turbidity, Pb, and Fe; PAC-ZC+HP > PAC-HP > PAC-ZC > PAC-D for Cu; PAC-D > PAC-ZC+HP > PAC-HP > PAC-ZC for Ni while Zn was insignificant. PAC-ZC and PAC-ZC+HP performed the best, although PAC-D has the highest BET surface area but was the least in heavy metal removal efficiency. The research has shown that activated carbon produced from Peat soil and treated with $ZnCl_2$ and $ZnCl_2$ + H_3PO_4 can be used for water treatment and heavy metal removal from produced water. This can be used to solve environmental problems resulting from improper handling and disposal of Oilfield Produced Water.

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The research should justify why the adsorption experiments were done at chosen conditions without optimization.

The researcher should improve on the tenses in reporting work already done. It should be in past tense

The researcher should improve on citing works that do not belong to him/her

The researcher should fit the data to test adsorption isotherms

Otherwise there is novelty in this research

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