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Batch adsorption using *C. aurantiifolia* peel as bio-adsorbent for the treatment of heavy metals in produced water from petroleum production

ABSTRACT

Most produced water treatment techniques are ineffective in reducing impurities and concentration of metals. This causes difficulty in achieving disposal levels. The effectiveness of a biomaterial for produced water treatment for a Niger Delta oilfield is presented. The produced water sample was collected from a Niger Delta oilfield and preserved at ambient temperature of 28 ^{o}C, further characterized, and the result showed lead (0.0082 mg/l). nickel (0.0084 mg/l), cadmium (0.0051 mg/l), copper (0.94 mg/l), iron (0.26 mg/l), magnesium (0.068 mg/l), chromium (0.0071 mg/l), zinc (1.17 mg/l) and manganese (0.053 mg/l). Citrus aurantiifolia peel was used as an adsorbent and it was purchased from a local market in Eziobodo, Nigeria. After peeling, the bioadsorbent (lime peel) was prepared by thoroughly washing it with distilled water to get rid of any extraneous materials (such as dirt or impurities) stuck on its surface. The washed lime peel was then cut to pieces and sun-dried for at least 48 hours, after which it was also oven-dried after preheating to 55^{o}C to prevent burning for 2-3 hours. The dried peels were then milled into finer particles, and packed in high-density polyethylene (HDPE, 0.77 mm thickness) bags. Experiments on batch adsorption were used to determine the effects of time of contact, dose of adsorbent, and speed of agitation. The samples were treated with the bioadsorbent on the magnetic stirrer in which various adsorption tests were carried out at different time intervals to obtain the optimum desired results for the removal of the metals. The Atomic Absorption Spectrophotometer technique was used in the study where the digested samples were analyzed for heavy metal content. Their concentrations were reduced after the treatments to Pb (0.0016 mg/l), Ni (0.0021 mg/l), Cd (0.00013 mg/l), Cu (0.019 mg/l), Fe (0.014 mg/l), Mg (0.0016 mg/l), Cr (0.0010 mg/l), Zn (0.21 mg/l), and Mn (0.0015 mg/l). The percentage of adsorption of Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, and Mn were 80.49%, 75.00%, 97.45%, 97.98%, 94.62%, 97.65%, 85.92%, 82.05%, and 97.17%, respectively. The Citrus aurantiifolia peels exhibited potential as adsorbent for heavy metals treatment in produced water.

Keywords: *heavy metals, produced water, Citrus aurantiifolia peel, bio-adsorbent*

1. INTRODUCTION

Produced water comes from the reservoir rock [1], and often produced with hydrocarbons [2]. It could also be injected water containing production chemicals and formation water [3], and the contents determine the treatment and handling method [1]. Organic and inorganic substances such as dissolved gases, formation minerals, production chemicals, dispersed oil compounds, and solids (asphaltenes, waxes, formation solids, and corrosion products) can also be found [2].

Permission is often given due salinity, treating chemicals, heavy metals, and radionuclides [2]. It can cause erosion [5] and makes up approximately 80% of residuals and wastes obtained during gas production [6]. For its prevention, (i) use of technologies to control its production, (ii) recycle and reuse, and if neither of the two steps above is feasible, (iii) disposal of the produced water is considered [2] are considered.

The highest estimates include the USA (21,000,000,000 bbl/yr.), Oman (1,840,000,000 bbl/yr.), Australia (207,570,000 bbl/yr.), Iraq (105,853,190 bbl/yr.), and China (45,917,000 bbl/yr.) [4]. Various management options exist [7], but re-injection is common [8]. Its use include petroleum industry and beyond [9], and quality values are given (Table 1).

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Table 1. Common produced water quality values in comparison with some criteria 10].

Parameter	End-use criteria (ppm)			CBM water	Non-CBM (Conventional gas well) water
	Drinking	Irrigation	Livestock		
pH	6.5-8	-	6.5-8	7-8	6.5-8
TDS, mg/L	500	2,000	5,000	4,000-20,000*	20,000-100,000
Benzene, ppb	5	5	5	<100	1,000-4,000
SAR*	1.5-5	6	5-8	Highly varied	Highly varied
Na^+, mg/L	200	See SAR	2,000	500-2,000	6,000-35,000
Barium, mg/L	-	-	-	0.01-0.1	0.1-40
Cl^-, mg/L	250	-	1,500	1,000-2,000	13,000-65,000
HCO_3^-, mg/L	-	-	-	150-2,000	2,000-10,000

*Total Dissolved Solids (TDS) range estimated for the lower 50 percentile

**Sodium Absorption Ratio (SAR) – a function of a ratio of Na to Ca and Mg levels

The water quality standards are comparatively lower for conventional gas wells when compared to drinking, livestock and other produced water reuse methods [11]. The heavy metals occur naturally in the subsurface and can be divided into three groups, (i) toxic metals; Sn, Co, As, Cd, Ni, Cu, Zn, Pb, Cr, Hg, etc, (ii) precious metals; Au, Ag, Ru, Pt, Pd etc, and (iii) radionuclides; Ra, U, Th, Am, etc. [1]. They can have effects on the soil, plants, aquatic environment, and human health [12]. Table 2 shows common heavy metals with maximum contamination levels (MCL) in water and their harmful effects.

Table 2. Harmful effects of the heavy metals [13]

S/N.	Heavy Metal	Maximum Contamination Level (mg/L)	Harmful Effects
1	Cu	0.25	liver damage, convulsions, insomnia.
2	Zn	0.80	skin irritation, nausea, depression, anaemia, and neurological symptoms.
3	Ni	0.20	carcinogen, dermatitis, gastrointestinal disorder, lung and kidney damage.
4	Cr	0.05	carcinogen, nausea, diarrhea.
5	Cd	0.01	carcinogen, kidney dysfunction.
6	As	0.05	skin problems, visceral cancer.
7	Pb	0.006	central nervous system damage, cerebral disorders, kidney, liver, and reproductive system dysfunction.
8	Hg	0.00003	neurotoxin, kidney dysfunction, circulatory and neurological disorders.

Adsorption is generally used for the treatment process because adsorbents can easily be overloaded with organics [14]. Also, adsorption isotherms and models give an estimate of the amount of adsorbate or solutes that have been adsorbed after adsorption has taken place per unit weight at constant temperature. The common models are Langmuir and Freundlich isotherms. Others include Redlich and Peterson, Sips, Radke and Prausnitz, Toth, and Koble, and Corrigan [13] [15]. Adsorbents could be natural or synthetic. Natural adsorbents include clays, charcoal, ores, zeolites, and minerals. Synthetic adsorbents are commonly prepared from agricultural and industrial wastes, etc. Some commonly used agricultural wastes and industrial wastes for the removal of heavy metals are shown in Table 3 and Table 4, respectively.

Adsorbent selection factors include high adsorbent capacity, low cost, and its effectiveness for a wide range of pollutants. Four identified efficient mechanisms for the adsorption of impurities/pollutants include physisorption, chemisorption, ion exchange, and precipitation. Similarly, functional groups in organic compounds [16] on carbon surfaces, such as *Citrus aurantiifolia* peel. These heteroatoms are surface functional groups [17]. Hydrogen bonding also bond electrostatically to other compounds [18]. Solute are also soluble due to forces that are large enough [19]. The oxygen functional groups determine the surface properties of a bio-adsorbent, and therefore the quality of the adsorbent [20]. The carboxyl and hydroxyl groups are great contributors to heavy metals adsorption such as Ni, Pb, Hg, Cd, and Cr ions onto a variety of carbon adsorbents such as the *Citrus aurantiifolia* [21].

Table 3. Common agricultural wastes for heavy metal removal [13]

S/N.	Type of Wastewater	Type of Adsorbent	Adsorbent Dosage (g)	Metal Ion	Amount Adsorbed (mg/g)	Contact Time (min)	Temperature (ºC)
1.	hospital wastewater	cassava peels	10.0	Pb^{2+} Cu^{2+}	5.80 8.00	20-120	39.85
2.	aqueous solution	ash gourd peel powder	6.0	Cr^{6+}	18.70	40-60	28.0
3.	aqueous solution	barley straw	1.0	Cu^{2+}	4.64	120	25.0
4.	aqueous solution	cashew nut	3.0	Ni^{2+}	18.86	30	30.0
5.	electroplating wastewater	chemically modified orange peel	2.0	Cu^{2+}	289.0	180	30.0
6.	aqueous solution	modified lawn grass	0.5	Pb^{2+}	137.12	400	29.85
7.	aqueous solution	grapefruit peel	2.0	U^{6+}	140.79	60-80	24.85
8.	aqueous solution	peanut shell	1.0	Cr^{6+}	4.32	360	30.0
9.	aqueous solution	sugarcane & orange peel biochar	1.0	Pb^{2+}	86.96 and 27.86	30	25.0
10.	electroplating wastewater	mango peel	5.0 5.0 5.0	Ni^{2+} Cu^{2+} Zn^{2+}	39.75 46.09 28.21	120	25.0
11.	aqueous solution	wheat shell	10.0	Cu^{2+}	17.42	60	25.0
12.	aqueous solution	sulfonated biochar	2.0	Pb^{2+} Cd^{2+}	191.07 85.76	5	180.0

Table 4. Common industrial wastes for removing heavy metals [13]

S/N.	Type of Wastewater	Type of Adsorbent	Adsorbent Dosage (g)	Metal Ion	Amount Adsorbed (mg/g)	Contact Time (min.)	Temperature (ºC)	pH
1.	dye and heavy metal wastewater	fly ash	2.0	Cd^{2+} Cu^{2+} Ni^{2+}	6.36 12.78 1.66	60	25.0	4.8-5.3
2.	aqueous solution	coal fly ash	2.5	Cu^{2+} Ni^{2+}	158.0 99.0	120 60	20.0	8.0
3.	aqueous solution	fly ash geopolymer	2.0	Cu^{2+}	152.0	120	45.0	6.0
4.	aqueous solution	fly ash bottom ash	2.0	Cd^{2+}	142.9 23.3	240	25.0	5.0-6.0
5.	aqueous solution	red mud	1.0	Cu^{2+}	5.3	60	30.0	5.5
6.	aqueous solution	activated red mud	4.0	Zn^{2+}	14.9	480	25.0	6.0
7.	aqueous solution	red mud	1.0	Co^{2+}	18.0	15	30.0	5.0
8.	aqueous solution	activated red mud	4.0	Pb^{2+}	6.0	30	30.0	4.0
9.	aqueous solution	basic oxygen furnace slag	0.5	Cu^{2+}	245.2	60	20.0	3.5
10.	synthetic water	LD slag geopolymer raw LD slag	2.0	Ni^{2+}	84.8 14.3	1440	45	10.0 10.0

Previous studies have shown that activated carbon have adsorption capacity up to 77.68% with oxygen functional groups onto the adsorption sites [22]. An adsorbent's surface area depends on how it's structured. As adsorption occurs, the carbon will usually experience expansion as a result of immersion, known as adsorption-swelling or adsorption-extension [23]. Also, (i) solids that are finely divided and (ii) porous substances are known to be good adsorbents [24]. Some researchers also suggest that the distribution of functional groups on an adsorbent surface depends on its pore size due to the presence of heteroatoms (usually oxygen, nitrogen, and sulfur) [25].

Activated carbon when used as adsorbents is not cost effective. An inexpensive adsorbent foundational material is the citrus fruits peel. They are of commercial value, readily available, and have average absorption capacity of 96% [26] [27]. Furthermore, study shows that agricultural materials contain lignin, protein, and polysaccharides which are linked with some functional groups and function as adsorbents for metal ions [28], with citrus peel regarded as one of the most important low-cost adsorbents [29]. This is due to their strong potential in the adsorption process due to their pectin (galacturonic acid), high content of cellulose, hemicellulose, and lignin [28]. Citrus fruits include orange peel, lime peel, lemon peel, etc. of the same genus of plant family group with similar biological, physical, and chemical properties. Their adsorption is through biosorption. The Freundlich Isotherm forms the basis for adsorption onto heterogeneous binding sites; the metal ions [27]. Biosorption is affected by the nature of the derived product or biomass, how it is applied, concentration, and surface area. The age, nutrition, and growth of the biomass also influence biosorption due to extracellular product formation, and changes in cell size, etc. [30].

2. MATERIALS AND METHOD

2.1. Materials

These include produced water samples from a Niger Delta oilfield and *Citrus aurantiifolia* peel (local adsorbent material). *Citrus aurantiifolia* is characterized by plant type (fruits, trees, shrubs), plant family (Rutaceae), genus (citrus), water needs (average), soil type (loam), soil pH (acid, neutral), soil drainage (moist but well-drained), and tolerance (clay soil). It grows under various climate zones under full sun exposure.

2.2. Method

2.2.1.Collection of samples/materials

The sample was collected from a Niger Delta oilfield (Fig.1) and preserved at ambient temperature of 28 ^{o}C. However, from multiple research analyses and tests, produced water commonly contains heavy metals such as Cd, Pb, Cu, Fe, Mg, Cr, Zn, and Mn. The adsorption experimentation and process would test for those ions. *Citrus aurantiifolia* peel (Fig. 2) was used as an adsorbent and it was purchased from a local market in Eziobodo, Nigeria.

Figure 1. Raw-produced water samples from the Niger Delta

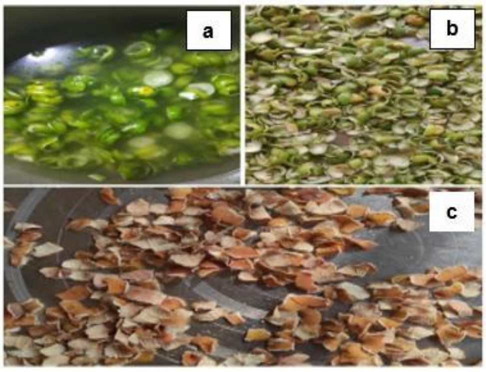

Figure 2. Raw Citrus aurantiifolia peel (local adsorbent material) (a) freshly peeled (b) initial drying stage (c) final drying stage

2.2.2. Atomic Absorption Spectrophotometer (AAS) technique and test procedure

The AAS technique was used in the study. The heavy metals were tested individually to first obtain the source absorbance value for each of the metals. These values were recorded and used as reference points through the adsorption experiment. The light absorbed by each metal, measured in nm, helps to determine the concentration amount of a metal in the solution. Three main parameters were considered for the AAS metal test procedure. Wavelength is the amount of light absorbed by a metal and the value of the wavelength is determined by the concentration amount of the metal in the solution. Slit allows for the entry of broad or narrow light wavelengths into the AAS monochromator and its width is expressed in mm. The detection limit is the highest/lowest signal or concentration of a metal that can be detected with the AAS method. For the experiment carried out it's also the sum of all the concentrations for each specific metal detected during the experimental procedure, from the highest to the lowest. Each metal was assigned different wavelength, slit & detection limit values according to when they get detected by the AAS due to the light absorbed by each respective metal for a given test.

The digested samples were analyzed for heavy metal content using Atomic Absorption Spectrophotometry (AAS) at a Research Laboratory in the Federal University of Technology, Owerri. The procedure involved aspirating the digested sample into an air-acetylene flame, where the solvent evaporated, and free metal atoms were vaporized in a process known as atomization. A hollow cathode lamp emitting light in the UV-visible spectrum was used to excite the metal atoms electronically. The absorbance of this light was then measured using a UV-visible dispersive spectrometer equipped with a photomultiplier detector. Each metal analysis was conducted in triplicate, and the instrument automatically provided the mean concentration values of the analyzed metals, including Lead, Nickel, Cadmium, Copper, Iron, Magnesium, Chromium, Zinc, and Manganese.

2.2.3 Preparation of Citrus aurantiifolia peel for experimental procedure

After peeling, the local adsorbent was prepared by thoroughly washing it with distilled water to get rid of any extraneous materials (such as dirt or impurities) stuck on its surface. The washed lime peel was then cut to pieces and sun-dried for at least 48 hours, after which it was also oven-dried after preheating to 55ºC to prevent burning for 2-3 hours. At that condition, the peels would have dried out and begin to curl or snap and don’t bend. This was done to reduce moisture content and adsorbed gases on the surface. The dried peels were then milled into finer particles (Fig. 3), and packed in high-density polyethylene (HDPE, 0.77 mm thickness) bags, and heat-sealed with a sealing machine to shield them from the external environment.

Figure 3. Finely grounded peel

2.2.3. Experiments performed with the adsorbent on the wastewater

Experiments on batch adsorption were used to determine the effects of these factors on the wastewater sample collected from the Niger Delta (Fig. 1).

i. Time of contact (mins.)
ii. Dose of adsorbent (g)
Iii. Speed of agitation (rpm)

1g of the *Citrus aurantiifolia* peel was added to a 50ml beaker with 30ml effluent-produced water with 7.1 as the initial pH. The beaker was kept on a magnetic stirrer at an ambient temperature of 30 ± 2°C. A speed of 150 rpm was maintained and agitated at a time interval of 5-60 mins for contact time effect. It was also aimed at determining the optimum time of the process of adsorption.

i. Effect of contact time

1g constant dose of the adsorbent (*Citrus aurantiifolia* peel) was stored in 18 polyethylene bottles which contain 30ml of the produced water. Agitation was achieved with a magnetic stirrer at 150 rpm and 5, 10, 15, 20, 25, 30, 40, 50, and 60-minute time intervals. The ambient temperature of 30 ± 2°C was recorded, and a pH of 7.1 was recorded. At the predetermined time intervals, the samples were collected from the stirrer and filtered. The filtrates were collected for further analysis.

ii. Effect of adsorbent dose

30ml of the effluents and 0.5, 1, 1.5, 2, 2.5, and 3g of the adsorbents were placed into 12 polyethylene bottles. They were agitated for 25 mins. and 30mins. optimum times for the bottle set that contains lime peels, respectively. It was performed at ambient temperature and a pH of 7.1. They were taken out of the stirrer and filtered. The filtrates were taken for further analysis. The percentage reductions in the pollution causative factors are calculated using Eq.1:

$$\% \text{ Reduction} = [(\text{initial conc.} - \text{final conc.}) / (\text{initial conc.})] \times 100 \qquad (1)$$

iii. Effect of agitation speed

Adsorbent selection factors include high adsorbent capacity, low cost, and its effectiveness for a wide range of pollutants. Four identified efficient mechanisms for the adsorption of impurities/pollutants include physisorption, chemisorption, ion exchange, and precipitation. Similarly, functional groups in organic compounds [16] on carbon surfaces, such as *Citrus aurantiifolia* peel. These heteroatoms are surface functional groups [17]. Hydrogen bonding also bond electrostatically to other compounds [18]. Solute are also soluble due to forces that are large enough [19]. The oxygen functional groups determine the surface properties of a bio-adsorbent, and therefore the quality of the adsorbent [20]. The carboxyl and hydroxyl groups are great contributors to heavy metals adsorption such as Ni, Pb, Hg, Cd, and Cr ions onto a variety of carbon adsorbents such as the *Citrus aurantiifolia* [21].

Adsorbent doses in the range of 0.5-3g were used and agitation speeds of 50-150rpm were also conducted for their effects. Whattman No.1 filter paper (pore size: 11µm particle retention) was used, and studies were carried out on the filtrates. Also, *Design-Expert® software version 13* was engaged. This software when applied established the optimum values and their treatment efficiencies. Finally, these optimum values were then re-visited experimentally to confirm them, and the kinetic parameter was established at those optimum values of the process variables.

3. RESULTS AND DISCUSSION

The wastewater was initially characterized, and the result showed lead (0.0082 mg/l). nickel (0.0084 mg/l), cadmium (0.0051 mg/l), copper (0.94 mg/l), iron (0.26 mg/l), magnesium (0.068 mg/l), chromium (0.0071 mg/l), zinc (1.17 mg/l) and manganese (0.053 mg/l). The CCD for each factor is also shown (Table 5).

There were three main factors included for each metal. They include (i) sample runs, (ii) concentration, and (iii) absorbance values (Table 6). The percentage reductions and AAS sample results are shown in Table 7. These three factors apply to all the nine metals used in the experimental procedure. The sample is also referred to as batch number. This describes the number of batch experiments/adsorption tests carried out for a particular metal. From the test, there were a total of 20 batch experiments.

Table 5. Central Composite Design (CCD) for each factor

Factor	Name	Axial low	Low	Mean	High	Axial High
A	Mass Dosage	0.727	0.50	6.00	1.00	12.727
B	Contact Time	9.546	30.00	60.00	150.00	110.454
C	Agitation Speed	331.821	600.00	500.00	900.00	668.179

Nine metals were constantly tested for every batch. Different values of three parameters that influence the adsorption process were assigned to each batch. The parameters are (i) mass dosage, (ii) contact time, and (ii) agitation speed. For example, in batch 1 (or sample run 1), a mass dosage of 6g, contact time of 60 mins, and agitation speed of 500 rpm were used as a constant assigned parameter value for each metal tested in batch 1. The varying adsorption results were then recorded for each respective metal. The AAS sample results and the standard chart for the metals are presented in Table 7 and Fig. 4. The calibrations of the heavy metals are shown with R^2 of Pb (0.994), Ni (0.997), Cd (0.981), Cu (0.997), Fe (0.993), Mg (0.993), Cr (0.993), Zn (0.987) and Mn (0.996).

3.1. Batch analysis result

Table 6. Design of experiment for heavy metals removal (concentration)

Runs	Mass Dosage (g)	Contact Time (Mins)	Agitation Speed (RPM)	Concentration								
				Pb (mg/L)	Ni (mg/L)	Cd (mg/L)	Cu (mg/L)	Fe (mg/L)	Mg (mg/L)	Cr (mg/L)	Zn (mg/L)	Mn (mg/L)
1	6	60	500	0.0038	0.0032	0.00014	0.038	0.038	0.0055	0.0026	0.74	0.0072
2	2	30	400	0.0026	0.0040	0.00037	0.041	0.041	0.0032	0.0019	0.57	0.0071
3	6	60	500	0.0019	0.0038	0.00024	0.036	0.025	0.0016	0.0015	0.38	0.0020
4	6	60	500	0.0025	0.0057	0.00016	0.081	0.051	0.0047	0.0015	0.32	0.0081
5	10	90	400	0.0044	0.0061	0.00028	0.053	0.036	0.0028	0.0037	0.46	0.0063
6	6	60	500	0.0031	0.0039	0.00035	0.019	0.052	0.0041	0.0025	0.31	0.0087
7	6	9.54622	500	0.0025	0.0034	0.00026	0.037	0.017	0.0033	0.0010	0.63	0.0072
8	6	110.454	500	0.0040	0.0047	0.00031	0.042	0.028	0.0044	0.0041	0.69	0.0036
9	10	30	600	0.0048	0.0056	0.00032	0.037	0.046	0.0024	0.0016	0.27	0.0071
10	12.7272	60	500	0.0033	0.0064	0.00027	0.041	0.014	0.0034	0.0027	0.22	0.0058
11	8	60	500	0.0041	0.0031	0.00025	0.025	0.030	0.0048	0.0017	0.48	0.0089
12	6	60	331.821	0.0035	0.0042	0.00017	0.056	0.047	0.0043	0.0035	0.36	0.0020
13	2	90	600	0.0027	0.0037	0.00040	0.040	0.056	0.0028	0.0041	0.21	0.0051
14	2	30	600	0.0016	0.0050	0.00035	0.039	0.035	0.0041	0.0032	0.51	0.0021
15	10	30	400	0.0039	0.0045	0.00013	0.051	0.040	0.0039	0.0015	0.98	0.0015
16	6	60	668.179	0.0043	0.0040	0.00034	0.034	0.029	0.0035	0.0047	0.58	0.0063
17	4	60	500	0.0053	0.0039	0.00041	0.052	0.052	0.0018	0.0041	0.71	0.0037
18	10	90	600	0.0028	0.0021	0.00026	0.023	0.037	0.0022	0.0018	0.44	0.0043
19	2	90	400	0.0042	0.0032	0.00019	0.044	0.043	0.0023	0.0023	0.63	0.0074
20	0.727171	60	500	0.0034	0.0043	0.00024	0.047	0.031	0.0045	0.0040	0.62	0.0062

Table 7. Source data, concentration reduction and AAS sample results

Heavy metal		Pb	Ni	Cd	Cu	Fe	Mg	Cr	Zn	Mn
Source	Concentration [mg/L]	0.0082	0.0084	0.00510	0.940	0.260	0.0680	0.0071	1.17	0.0530
	Absorbance	0.5864	0.7263	0.5140	4.9526	9.5510	1.5848	0.5169	4.0782	0.9116
Concentration reduction [%]		80.49	75.00	97.45	97.98	94.62	97.65	85.92	82.05	97.17
AAS sample results										
Name		Pb	Ni	Cd	Cu	Fe	Cr	Zn	Mg	Mn
Wavelength, nm		283	341	228.9	324.8	248.3	357.9	213.9	285.2	279.5
Silt, nm		0.7	0.2	0.7	0.7	0.2	0.7	0.7	0.7	0.7
Detection limit, mg/l		0.08	0.1	0.01	0.005	0.05	0.04	0.005	0.005	0.03

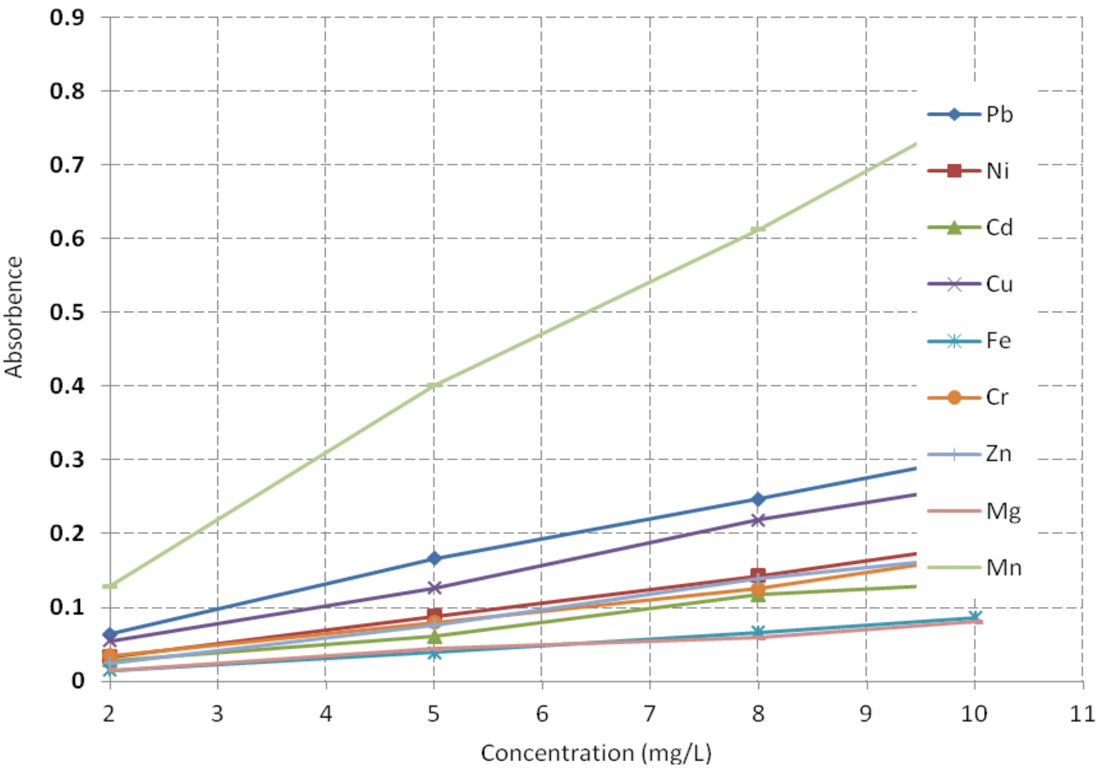

Figure 4. Standard chart for the heavy metals

Concentration is the second factor for each metal. This describes the concentration amount of the metal left after the adsorption of that batch has taken place. There's a sub-factor known as the "source". For the section on concentration factor, the source indicates the initial concentration of the metal before any batch adsorption was carried out. It's recorded for each metal and it's a constant value that's compared to every batch. The metal concentration amount left in the produced water after batch adsorption is completed is usually compared to the source concentration to deduce the percentage reduction of that metal for the respective batch. For example, the concentration of lead metal Pb in batch 1 (or sample run 1): was reduced from its source concentration, 0.0082 mg/L to 0.0038mg/L. In Batch 2, it was reduced from a source concentration of 0.0082mg/L to 0.0026mg/L, etc. After 20 runs or batch adsorption were conducted, Pb was best reduced to its lowest concentration of 0.0016 mg/L in batch 14 when compared to the other batches. That yielded a concentration reduction of 80.49% as shown in Table 7. Similar observations were made for the other heavy metals.

Similarly, absorbance values, measured in AU (absorbance unit), at every numbered row (batch number) were recorded. This describes the quantity of light absorbed by each metal when tested in the AAS after the adsorption process of that batch has taken place. The sub-factor known as "source" also applies to this. For the section on absorbance value, the source indicates the initial absorbance of the metal before any batch adsorption was carried out. It's recorded for each metal and it's a constant value that's compared to every batch. The closer the absorbance value is to 1.0 or greater than 1.0, it's an indication of the high concentration amount of that metal.

20 runs were performed on the wastewater to obtain optimum results. From the batch adsorption results obtained during the experiment, the concentration of heavy metals in the produced water was successfully reduced. Moreover, this reduction is affected by three main parameters. They include mass dosage (g), contact time (mins), and agitation speed (rpm). It is observed that each of these parameters has a different concentration reduction effect on each of the metals that were tested. On the 14th run, Pb had the lowest concentration value of 0.0016 mg/L at an agitation speed of 600 rpm using an adsorbent mass dosage of 2g for 30 minutes. The traces of Ni dropped to the lowest (0.0021) with an agitation speed of 600 rpm using a mass dosage of 10g for 90 minutes and this was achieved in the 18th run. The lowest concentration value of Cd was 0.00013 using 10g of mass dosage for 30 minutes with a 400 rpm on the 15th run. Cu was also reduced to a low value of 0.019 mg/L after agitating with a speed of 500 rpm for 60 minutes at an adsorbent dosage of 6g. The concentration of Fe decreased to 0.014mg/L with the highest dosage amount of 12.73g used in the 10th run at a speed of 500 rpm for 60 minutes. The 3rd run produced the lowest value 0.0016 mg/L of Mg with a mass dosage of 6g and, a contact time of 60 minutes at 500 rpm. The level of Cr dropped to its lowest (0.0010) during the 7th run with an agitation speed of 500 rpm and, an adsorbent mass dose of 6g for 60 minutes. Zn and Mn had a low of 0.21 and 0.0015 with agitation speeds of 600 and 400 rpm, and mass dosages of 2g and 10g for 90 and 30 mins on the 13th and 15th runs, respectively.

The lowest concentrations of heavy metals were achieved at varying agitation speeds, contact times, and adsorbent mass doses. It proved the advantage of the batch adsorption process for optimal results. From the experiment, the best value of the adsorption parameters obtained during the experiment for an effective reduction of each of the heavy metals using *Citrus aurantiifolia* peel as an adsorbent is given in Table 8.

Table 8. Adsorption parameters for an effective reduction of heavy metals

Name	Agitation speed, rpm	Mass dosage of adsorbent, g	Contact time, min.
Pb	600	2	30
Ni	600	10	90
Cd	400	10	30
Cu	500	6	60
Fe	500	12.73	60
Mg	500	6	60
Cr	500	6	60
Zn	600	2	90
Mn	400	10	30

With the specific parameters, the metal concentrations in the water sample with Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, and Mn were decreased from 0.0082, 0.0084, 0.0051, 0.940, 0.260, 0.0680, 0.0071, 1.17 and 0.053 to 0.0016, 0.0021, 0.00013, 0.019, 0.014, 0.0016, 0.0010, 0.21 and 0.0015, respectively.

4. CONCLUSION

The procedures involve the use of standard solutions prepared at ambient temperature in the laboratory. The produced water samples had impurities and traces of heavy metals. All experiments were performed at ambient temperature, while the parameters considered during the tests were time, mass dosage of adsorbent, and agitation speed. The tests were carried out at a constant temperature, and reduction of the heavy metals' concentration at ambient temperature at varying time intervals, mass dosage, and agitation speed. The Atomic Absorption Spectrophotometer was used to detect the concentration of the metals treated with the local bio-adsorbent. Also, the research showed that the concentration of the heavy metals was in excess as compared to allowable values for re-use or discharge. After the produced water samples were treated with the local bio-adsorbent in the batch adsorption process, metal concentration was reduced to the desired values in the samples. The percentage of adsorption of Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn, and Mn were 80.49%, 75.00%, 97.45%, 97.98%, 94.62%, 97.65%, 85.92%, 82.05%, and 97.17%, respectively. Time was considered a major parameter since it was required for effective adsorption. It is concluded that the bio-nature of the adsorbents such as *Citrus aurantiifolia* and orange peels which are agricultural wastes, as observed by other researchers, have high amounts of cellulose, tannin, hemicelluloses, and lignin. Similarly, they have fibrous materials and functional groups which immensely contribute to adsorption from fresh water. The contents of these materials enable them to effectively bind metal ions. Hence, the adsorbent used has excellent binding abilities.

Conflict of interest

No known conflict of interest has been declared by the authors.

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IZVOD

ŠARŽNA ADSORPCIJA KORIŠĆENJEM KORE *C. AURANTIIFOLIA* KAO BIO-ADSORBENTA ZA TRETMAN TEŠKIH METALA U PROIZVEDENOJ VODI IZ PROIZVODNJE NAFTE

Većina tehnika tretmana proizvedene vode je neefikasna u smanjenju nečistoća i koncentracije metala. Ovo uzrokuje poteškoće u postizanju nivoa odlaganja. Prikazana je efikasnost biomaterijala za tretman proizvedene vode za naftno polje delte Nigera. Uzorak proizvedene vode je sakupljen sa naftnog polja Delta Nigera i čuvan na temperaturi okoline od 28^{o}C, dalje karakterisan, a rezultat je pokazao olovo (0,0082 mg/l). nikl (0,0084 mg/l), kadmijum (0,0051 mg/l), bakar (0,94 mg/l), gvožđe (0,26 mg/l), magnezijum (0,068 mg/l), hrom (0,0071 mg/l), cink (1,17 mg/l) i mangan (053 mg/l). Citrus aurantiifolia kora je korišćena kao adsorbent i kupljena je na lokalnom tržištu u Eziobodu, Nigerija. Nakon ljuštenja, bioadsorbent (limetova kora) je pripremljen temeljnim pranjem destilovanom vodom da bi se uklonili svi strani materijali (kao što su prljavština ili nečistoće) zaglavljeni na njegovoj površini. Oprana kora limete je zatim isečena na komade i sušena na suncu najmanje 48 sati, nakon čega je, takođe, sušena u rerni nakon zagrevanja na 55^{o}C da bi se sprečilo zagorevanje 2-3 sata. Osušene kore su zatim mlevene u sitnije čestice i pakovane u kese od polietilena visoke gustine (HDPE, debljine 0,77 mm). Eksperimenti sa šaržnom adsorpcijom su korišćeni da bi se odredili efekti vremena kontakta, doze adsorbenta i brzine mešanja. Uzorci su tretirani bioadsorbentom na magnetnoj mešalici u kojoj su vršeni različiti testovi adsorpcije u različitim vremenskim intervalima da bi se dobili optimalni željeni rezultati za uklanjanje metala. Tehnika atomskog apsorpcionog spektrofotometra je korišćena u studiji gde su digestirani uzorci analizirani na sadržaj teških metala. Njihove koncentracije su nakon tretmana smanjene na Pb (0,0016 mg/l), Ni (0,0021 mg/l), Cd (0,00013 mg/l), Cu (0,019 mg/l), Fe (0,014 mg/l), Mg (0,0016 mg/l), Cr (0,0010 mg/l) i Mn2 (0,0010 mg/l). (0,0015 mg/l). Procenat adsorpcije Pb, Ni, Cd, Cu, Fe, Mg, Cr, Zn i Mn bio je 80,49%, 75,00%, 97,45%, 97,98%, 94,62%, 97,65%, 85,92%, 82,05%, odnosno 97,17%. Citrus aurantiifolia kore su pokazale potencijal kao adsorbent za tretman teških metala u proizvedenoj vodi.

Ključne reči: *teški metali, proizvedena voda, kora Citrus aurantiifolia, bio-adsorbent*

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