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Adsorption of Toxic Water Pollutants Using Modified Groundnut Shell

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ABSTRACT
Bioremediation of toxic industrial effluents by engineered processes serves as an effective method to replace the conventional recovery of contaminated soil, surface and ground water bodies and the restoration of same to a stable condition that support life. Plant materials (groundnut shell) activation capability for treating effluent discharge from industries is explored in this paper. Activated Groundnut shell was examined in adsorption of heavy metals such as Copper (Cu), Magnesium (Mg), Iron (Fe) and Chromium (Cr) in an industrial effluent discharge. The trend of the sorption capacity was found to be Fe>Cr>Cu>Mg for groundnut shell in the order of 100%, 98%, 70%, and 9% respectively. This study is a prognosis into the capacity of plant substrate in bioremediation of polluted soils and groundwater reducing different heavy metals in the stream effluent.
Keywords: *Bioremediation, toxic effluent, groundnut shell and Sorption capacity.*

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I. INTRODUCTION

Industrialization and Urbanization has greatly exposed our rivers and streams to great danger of pollution through toxic effluent discharges from industries and household chores. Consequent upon the environmental degradation suffered, huge economic resources and operational costs are the attendant features of the conventional waste management processes to stem the losses. This has remained a great challenge to scientists and engineers alike the world over.

1.1 Metals Toxicology

Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other breakdown or degradation process and are permanent additions to the marine environment [1]. Their concentrations often exceed the permissible levels normally found in soil, waterways and sediments and by extension in the food pyramid. When they accumulate in the environment and in food chains, they can profoundly disrupt biological processes in human anatomy, and with damaging consequences [2]. Among other health implications of heavy metals accumulation in humans include kidney dysfunction, hepatic damage and hypertension [3]. Toxic levels of lead (Pb) in man have been associated with encephalopathy, seizures and mental retardation. The presence of copper (II) ions causes serious toxicological concerns. It is usually known to deposit in brain, skin, liver, pancreas and myocardium [4]. Mercury pollution results from metallurgical industries, chemical manufacturing and metal finishing industries [5]. Mercury in the liquid form is not dangerous but becomes very poisonous in its vapour form. It attacks the lungs, kidneys and the brain. The vapour closes the blood-brain and blood stream [6]. Arsenic affects the skin causing skin cancer in its most severe form. A massive outbreak of arsenical dermatitis which was reported in some parts of West Bengal State of India was linked with high levels of arsenic in tube well waters (0.2 - 2.0 mg/l) [7]. In the recent time, lead poisoning from mining sites is a health issue that affected several children in northern part of Nigeria.

An ideal waste treatment process must completely mineralize or neutralize the toxic species present in the waste streams without leaving behind any hazardous residues and the process should be cost-effective.

Improvement of metal adsorption from an industrial effluent by using several modification approaches on agricultural products such as Groundnut shell as adsorbent was investigated in this paper. The adsorbent was first modified by slightly altering the surface area of the activated adsorbents by a sequence treatment with nitric (HNO_3) acid and sodium hydroxide (NaOH).

1.2 Kinetics of Adsorption

Adsorption is defined in two ways; one is physico-sorption which is due to forces of physical nature called Van der Waals forces in which adsorption is relatively weak and plays less important part in connection with surface reactions because they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is known as chemisorption. In this process, the adsorbed molecules are held to the surface by valence forces of the same type as those occurring between bound atoms in molecules. The heat evolved is of the order 10 to 100 kcal per mole, compared to physico-sorption which has less than 5 kcal per mole [8]. Literature showed that chemical signature (cellulose, hemicelluloses and lignin) and structural matrix of the plant substrates plays important role in the sorption of the metals through ion exchange. Intracellular physical sequestration of metal by binding to the ligands to the substrates thus preventing the metal burden in sensitive cellular targets through a mechanism which does not allow by allowing metal sequestration into vacuolar compartment

1.3 Conventional Methods

Adsorptive removal of heavy metals from aqueous effluents which have received much attention in recent years is usually achieved by using activated carbon or activated alumina [5, 9, 10, 11]. Activated carbon is a porous material with an extremely large surface area and intrinsic adsorption to many chemicals. The conventional adsorbents are the polymer resins that can form complexes with the heavy metal ions and many others have been reported such as silica gel, active alumina, zeolite, metal oxides [8] and so on. They are the best adsorbents. These conventional adsorbents are employed in many processes for the removal of heavy metals from wastewater such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, reverse osmosis, ion exchange and membrane technologies [12]. These processes are, however, associated with issues and constraints [13]. Among the issues is that activated carbon is only able to remove around 30-40 mg/g of Cd, Zn, and Cr in water and is non-regenerable which is quite costly to wastewater treatment [14]. A major drawback with precipitation is sludge production and its attendant cost of removal. Ion exchange is considered a better alternative technique, but it is not economically appealing because of high operational cost. A noteworthy constraint in the conventional adsorption process is that the particle-size of the adsorbent is restricted because of hydrodynamic phenomena such as pressure drop [15]. With these issues and constraint, biological methods such as bio-sorption/bio-accumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods. Bio-sorption or bioremediations consists of a group of applications which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants. This process is characterized as less disruptive and can be often carried out on site (in-situ bioremediation), eliminating the need to transport the toxic materials to treatment sites [16]. Bio-sorbents are prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and very cost-effective source of the raw material, bio-sorption is a progression towards a perspective method. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown levels of metal uptake high enough to warrant further research [13]. Bio-sorbents of plant origin are mainly agricultural by-products such as, Maize cob and husk [5] Sunflower stalk [14], sawdust [5], Chitosan [17,18] Shea butter seed husks[19], Banana pith, Coconut fiber, Sugar-beet pulp, Wheat bran[20] and sugarcane bagasse [21] among others.

II. MATERIAL AND METHOD

2.1 Material Source

The wastewater analyzed was obtained from the effluent discharge into the Ikeja, Lagos Nigeria central sewage treatment unit. The samples were collected and analyzed for the presence magnesium (*Mg*), copper (*Cu*), chromium (*Cr*) and iron (*Fe*). The environment is characterised by industrial activities with notable volumes of effluent discharges into the canals. The biomass, Groundnut shell, used was obtained from the process of extracting edible groundnut oil.

2.2 Material processing

The biomass was pre-treated by repeated washing with distilled water until to eliminate deleterious impurities following which it was oven dried for 48 hours. It was then crushed and sift to obtain a desirable storable powder of granulometry ranging from 100 to 700 micrometers. In chemical treatment, the dried biomass was introduced into a solution of hydroxide sodium of 0.01M concentration. The biomass is maintained in suspension during which the vessels were rigorously mixed using a stirrer equipped in the system for 30 min at ambient temperature and repeatedly filtered and washed with distilled water. It was then oven dried at 50°C for two hours and thereafter filtered. The dried biomass was stored in a desiccator and used as bio-sorbent in the sorption experiments. All chemicals used in this study were of analytical grade. In order to adjust the pH, 0.1 M HCl solution was used. Metal determination in the effluent extract was carried out by means of atomic absorption spectrophotometer (Model Solaar 969, ATI Unicam Comp.) equipped with a digital direct concentration read out and an air–acetylene burner using single element hollow cathode lamps (ATI Unicam Comp.). When the concentrations were under the detection limit of flame, the AAS external standards in diluted acid were used to calibrate the accuracy of atomic absorption. The yielded adsorbents were divided and chemically modified in different approaches: by reaction with 1M citric acid (CA-C) and subsequently with 1M sodium hydroxide (CA-SC), by oxidation with concentrated of nitric acid (NA-C) and subsequently by reaction with 1M sodium hydroxide (NA-SC): A value range of 0.5mg to 1.5mg of the substrate was added to 100ml flask of the prepared sampled effluent. Each sample was set at different contact range of 15minutes up to a 2hr period at which the solutions were rigorously stirred. Each sample was filtered using Whitman filter paper and the residual solution again analyzed for metal concentration. The relative adsorption of the metals into the substrates was calculated using the mathematical balance equation:

$$q_a = \frac{(C_o - C_f)\,v}{m} \qquad (1)$$

where q_e is the amount of the corresponding metal adsorbed into the adsorbent (mg/g); C_o is the initial metal ion concentration (mg/L); C_f is the final metal concentration at in the solution (mg/g) at equilibrium; v is the volume of the solution (L) and m is the mass of adsorbent (g)

Results and Discussion of results

Adsorbent dose of 1.0 g/100ml of the sample was chosen for analysis because of the erratic nature of results obtained for the other two doses of 0.5 g/100ml and 1.5 g/100ml. The effect of pH concentration on the adsorption of metals was not investigated (i) for the fact that increasing the pH will facilitate the precipitation of metal hydroxides and (ii) owing to the fact the experiment was a preliminary investigation into the suitability of the substrate and the otherwise consideration will be akin to the parameter estimation of the adsorption isotherm which will be a subject of discussion in the subsequent paper. However, it was established from the figures (fig. 1-5) that maximum adsorption (above 85%) for the metals occurs at the initial time contact except for magnesium. The relatively constant value beyond 20 minutes may be due to lowering of driving force and equilibrium attained between the adsorbent and the adsorbate at that temperature. Figures 1-5 shows comparative adoption of the metals into the groundnut shell at various contact time relative to their initial concentrations in the sampled waste. Magnesium adsorption increases with time up to the 28th minute followed by a sharp regression up to the 60th minutes while Copper showed a gradual decline of adsorption 2.72mg/l and the graph asymptotic to 2.85mg/l adsorptive capacity. Chromium has constant maximum adsorptive value of 0.58mg/l through the experimental period while Iron has a 100 percent approximate (5.8mg/l) of its initial concentration.

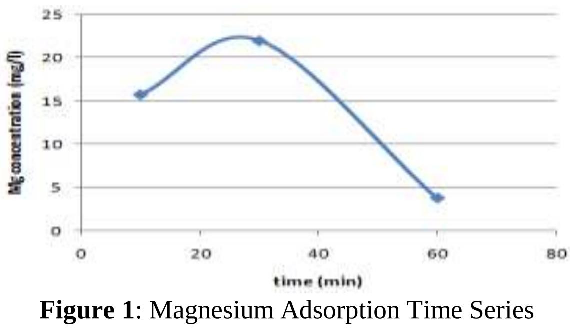

Figure 1: Magnesium Adsorption Time Series

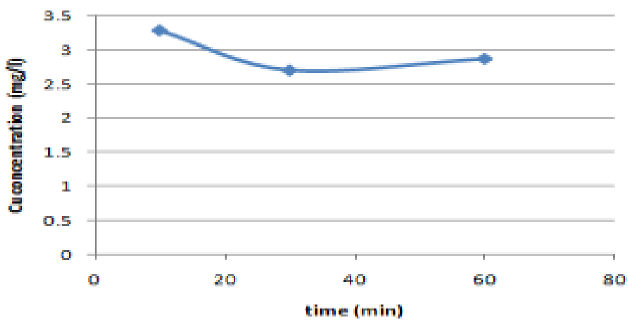

Figure 2: Copper Adsorption Time Series

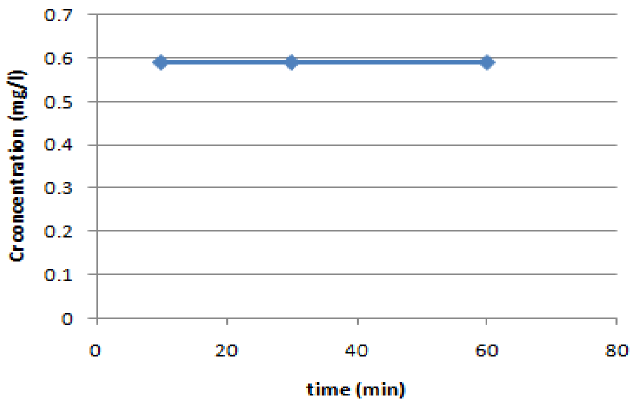

Figure 3: Chromium Adsorption Time Series

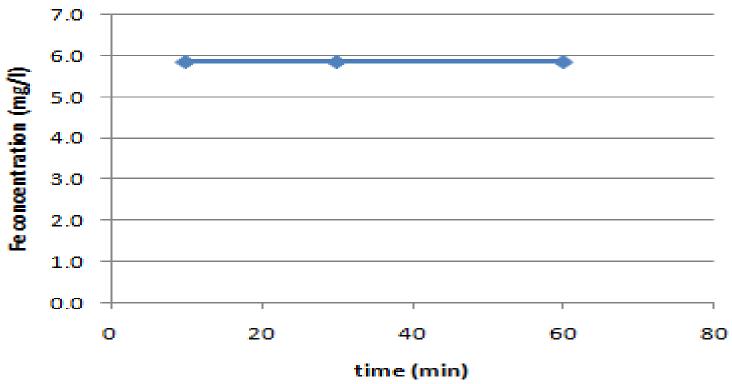

Figure 4: Iron Adsorption Time Series

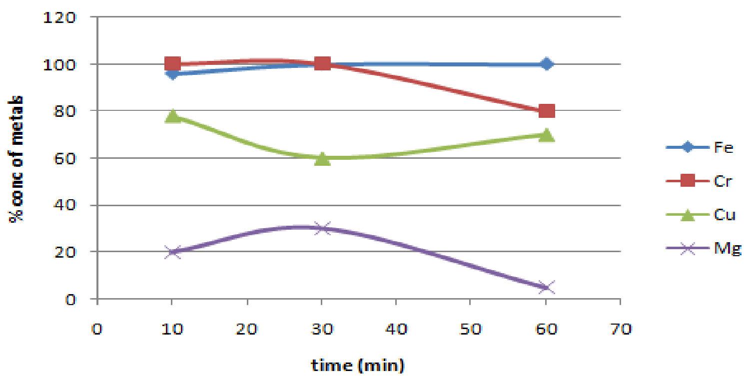

Figure 5: Percentage concentration of Metals Adsorbed to Substrate

III. CONCLUSIONS AND RECOMMENDATIONS

Groundnut shell is a good adsorbent of Fe and Mg. The trend of uptake for groundnut shell is in the order of Fe> Cr >Cu >Mg. Groundnut shell which is a waste has been applied in the partial treatment of toxic wastewater which is a major problem to civil engineers in the remediation of water pollution problems. Also the result of this experiment can be used as a parameter to reduce the weakening effect which some of those toxic metals have on water and/or effluent carrying pipes. Since some metals in water reduce the compressive strength of concrete, the removal or reduction of these metals using cheap absorbents such as the ones used in this experiment and /or more agricultural by-products that are yet to be unveiled will reduce the cost of construction in toxic areas. This experiment forms the basis for the study of kinetics of adsorption capacity of groundnut shell with the view of varying other parameters such as the pH, temperature, the adsorbent dosage, contact period in order to establish the level of its performance and adsorption isotherm parameter. The study showed that modified plant residue like groundnut shell has the potential to be used as an adsorbent material for removal of heavy metals from industrial effluent before discharging into the water body.

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