Adsorption of Cd (II) Ions from Aqueous Solution Using Activated Carbon Prepared from *Vitellaria paradoxa* Shell

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ABSTRACT

Activated carbon prepared from *vitellaria paradoxa* shell using ortho-phosphoric acid as activating agent was used for the removal of Cd (II) ions from aqueous solution. The adsorbent was characterized by some physicochemical and spectroscopic methods such as pH, point of zero charge (PZC), moisture content, iodine number, loss on ignition, bulk density, XRF, SEM and TEM. The pH and PZC of the sample were found to be 4.0 and 5.8 respectively. The adsorbent sample has moisture content of 5.22 ± 0.1%, iodine number of 256.50 ± 59%, loss on ignition of 10.71 ± 0.18% and bulk density of 0.84 ± 0.09%. The XRF analysis indicated that Ca, Si and Fe were major constituents in the adsorbent sample. The morphology of the adsorbents as revealed by SEM and TEM analysis results indicated good adsorptive characteristics of the adsorbent. The equilibrium adsorption of Cd (II) ions data were well fitted with Langmuir and Freundlich isotherms with correlation coefficient of 0.996 and 0.998 respectively. The kinetics study revealed that the experimental data fitted pseudo-second order kinetic better when compared to zero-order kinetics. Thermodynamics experiment indicated that the adsorption process was endothermic with ΔH value of +27.84 kJ/mol and ΔS of +0.993 kJ/molK and ΔG is negative at all temperature indicating the feasibility of the adsorption process.

Keywords: *Vitellaria paradoxa,* adsorbent, adsorption, SEM and TEM, heavy metals, kinetics, thermodynamics

1.0 INTRODUCTION

Cadmium is released by various natural and anthropogenic sources to the atmosphere, aquatic environments (fresh and salt water environments) and terrestrial environments.

In the environment, cadmium is toxic to plants, animals and micro-organisms. Being an element, cadmium is persistent – it cannot be broken down into less toxic substances in the environment. The degree of bioavailability and potential for effects varies depending on the form of cadmium.

Because of its toxicity and bioaccumulation, Cd (II) is considered as a priority pollutant by the U S Environmental Protection Agency. The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm^3. The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries (Cheremisinoff, 1995).

The shea tree (*Vitellaria paradoxa*) is found in areas with 400-1800 mm rainfall per year. It is a multi-purpose tree daily used by rural African communities. The fruit when ripe is either eaten as a snack and also as a famine food. It can be eaten raw or slightly cooked. The pulp can be processed into juice. According to McAllan *et al*. (1996), the pulp could also be removed by fermentation. The nuts are laid out to dry in the sun. The kernels are extracted usually before the butter making starts, by cracking open the nuts with stones or gently pounding in a mortar and the powder is made into butter.

This study investigated the potential of the *Vitellaria paradoxa* shell which are agricultural waste as adsorbent for the removal of Cd(II) ions from aqueous solution.

2.0 MATERIALS AND METHODS

2.1 Activated Carbon preparation

The Shea nut shells (*vitellaria paradoxa*) were collected from a small scale Shea butter producing factory at Budo oja at Ifelodun L.G.A. area in Kwara state. The sample was washed with plenty of water to remove surface impurities and sundried. Sample was later dried in an oven at 105^{O}C overnight (Fan *et al*., 2003, Mozammel *et al*., 2002, Zahangir *et al*., 2008, Itodo *et al.,* 2009 and Omonhenle *et al.,* 2006). A 100g of pre-treated sample (< 2mm mesh size) was introduced into a clean and pre weighed crucibles and carbonized in a furnace at 500^{O}C for 5 minutes and washed with cool water and 10% HCl to remove surface ash. Accurately weighed 3g carbonized sample was mixed with 2cm^3 of each 1M activating agent (H_3PO_4). The sample was introduced into a furnace, heated at 800^{o}C for 15 minutes. The activated sample was cooled with ice cold water. Excess water was drained and sample was allowed to dry at room temperature (Gimba *et al.*, 2004).

2.2 Sample preparation

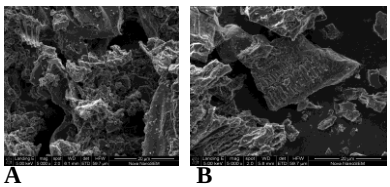
The stock solution of $CdSO_4$ was prepared and diluted into the required concentration using de-ionised water whenever necessary.The adsorption to equilibrium time was determined using 0.1 g of activated vitellaria paradoxa, 50 mL of metal solution with a concentration of 200 mg/L. The mixture was shaken (120 rpm) for 2 hours at ambient temperature. The amount of heavy metal adsorption per unit weight of activated *vitellaria paradoxa* at time *t* (q_t) in (mg/g), was calculated. Adsorption isotherms of the heavy metals were determined by varying the initial concentration of the metal solutions in range of 10-200 mg/L at constant and time.

3.0 RESULTS AND DISCUSSION

3.1 Physico-chemical properties of adsorbents

The moisture content of the activated carbon sample was 20.20% which suggested extensive porosity in the structure of adsorbent (Suguvadevi *et al*., 2002).

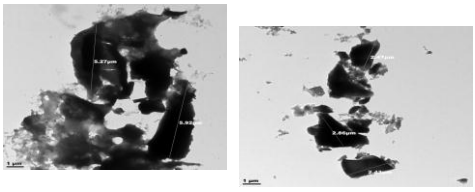
The percentage ash content was 10.71% for activated carbon sample which indicated a decrease in percentage volatile matter (Gan *et al*., 2004). The pH of the activated adsorbent after mixing with de-ionised water was 4.0 which might be the kind of treatment to which the adsorbent was subjected. The result of the iodine number of the activated carbon sample was 256.2 indicating good adsorptive capacity and better development of the microporous structure (Aziz *et al*., 2009; Baccar *et al.,* 2009).The SEM of the adsorbent showed rough areas of surface of the carbon and very minute micropores (figure 1).



A **B**

Figure 1. SEM Micrograph of activated carbon sample (A) and SEM Micrograph of activated sample after adsorption (B)

Transmission electron microscope (TEM) was used to determine the internal morphology of the adsorbent. It was observed (figure 2) that the adsorbent was effective on Cd adsorption, since the internal pore sizes was reduced in Cd-embedded adsorbent.



A B

Figure 2.TEM Micrograph of activated sample(A) and TEM Micrograph of activated sample after adsorption(B)

The elemental analysis by XRF of the adsorbent result showed that Ca, Si and Fe are present as major constituents (1.528- 12.18%); Na, Ti and Zn are minor constituents (0.36-0.6775%) while Mg, Al, P, Mn, Co, Ni, Cu and Cd are in traces (0.0018-0924%).

The pH_{pzc} was found to be 5.8 for the activated carbon while its pH was 4.0 indicating that the adsorption of anions could be enhanced (Hamadaoui, 2007; Almeida *et al*., 2009 and Farahani *et al*., 2011

3.2 Batch Adsorption Studies

The degree of metal ions adsorption onto the adsorbent increased from 50.48mg/L to maximum of 57.37mg/L of Cd(II) when the solution pH was increased from 2-6(Sari and Tuzen, 2009). The maximum percentage removal of 87.37% of Cd (II) was observed at 0.1g. The results were subjected to Langmuir and Freundlich adsorption isotherm models. The correlation coefficient of 0.996 and 0.998 were obtained for Cd(II) indicating monolayered multilayer adsorption nature of Cd (II) ions. The pseudo-first order plot is linear with correlation coefficient of 0.361. The pseudo-second order kinetic plot is of better linearity with correlation coefficient 0.97. The ΔG value of Cd (II) was negative, confirming the thermodynamic feasibility of adsorption of Cd (II) on *Vitellaria paradoxa* (Chowdhury *et al*., 2011).

4.0 CONCLUSION

The equilibrium adsorption data for the removal of Cd(II) ion from aqueous solution showed satisfactory correlation with the Langmuir adsorption and Freundlich. The kinetic study revealed that pseudo-second order kinetic was better fitted compared to first-order kinetic. Thermodynamic study revealed a spontaneousity of the process.

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