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An Evaluation of the Removal of Progesterone in Wastewater by Adsorption onto Waste Tea Leaves

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***Abstract*— The removal of endocrine disrupting chemical progesterone by adsorption onto waste black tea leaves was investigated in laboratory-scale experiments. The removal efficiency was compared with the widely used granular activated carbon (GAC). The performance of waste black tea leaves for the adsorption of progesterone was found to be comparable to conventional GAC. The maximum adsorption capacities for tea leaves and GAC were 1.8 mg/g and 1.4 mg/g respectively. The values for the thermodynamic parameters associated with sorption of progesterone onto tea leaves were Gibb's free energy (-6.0 KJ/mol), enthalpy (-3.7 KJ/ mol) and entropy (8.0 J/mol K), indicating that the sorption process was favorable, spontaneous and involved physical adsorption held by Van der Waal forces. The adsorption was guided by diffusion within the pores of the tea leaves.**

Keywords— Adsorption, GAC, Progesterone, Black Tea Leaves

I. Introduction

Endocrine Disrupting Chemicals (EDCs) are of increasing concern in recent times, as they pose a threat to human health and the environment [1, 2]. These chemicals are capable of impacting negatively on the endocrine systems of humans and wildlife [3]. There is a wide range of endocrine disruptors which are present in the environment, natural and synthetic. EDCs are mainly released by humans, animals, and industries into the environment through sewage treatment plants and agricultural runoffs [4, 5, 6].

Conventional wastewater treatment processes are usually not adequate in removing these EDCs to potentially no-effect concentrations [6]. Adsorptions onto various adsorbents have been investigated as options for their removal from wastewater. The adsorption process has a wide range of advantages over other treatment methods due to its applicability at very low concentrations, suitability for batch and continuous processes, ease of operation, possibility of regeneration and reuse of the adsorbents as well as lower capital cost and environmental sustainability.

Several adsorbents have been used for the removal of different EDCs in wastewater treatment applications. Activated carbon (AC) has been investigated considerably, as an adsorbent for the removal of EDCs from water and wastewater [7, 8, and 9]. The use of AC is often limited by its relatively high cost.

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Various researchers have investigated alternative low cost adsorbents such as peat, sawdust, bagasse, rice husk [10], carbon nanotubes [11, 12, 13], imprinted polymers [14], zeolites [15], Pine bark, almond shell [16] and waste tea leaves [17], as adsorbents for the removal of organic and emerging contaminants in water and wastewater. This study was carried out to evaluate the adsorptive properties of waste black tea leaves for the removal of progesterone in wastewater effluent. The performance of black tea leaves was also compared with that of granular activated carbon (GAC).

II. Materials and Methods

A. *Materials*

Analytical grade methanol, sodium hydroxide (NaOH) and ortho-phosphoric acid were purchased from Fisher Scientific (UK), progesterone was obtained from Sigma-Aldrich (UK). A readily available box of English Breakfast tea (~750 g) was purchased from a local supermarket. Stock solutions (~1 g/l) of progesterone were prepared in 100% methanol and serial dilution carried out to attain the calibration curve. The standards were stored in the fridge <4°C until needed. The analysis was carried out using external calibrations with a concentration range of 0.5 – 2 mg/l. The treatment of the black tea leaves and the batch adsorption experiments have been previously described by Ifelebuegu et al. [17]. The characteristics of the GAC used have been reported elsewhere [9].

B. *Batch Adsorption Studies*

The batch adsorption experiments were carried out using the bottle point method as has been previously described by Ifelebuegu et al. [17]. The absorbent coefficient was determined using the equation:

$$q_e\ (mg/g) = \frac{C_o - C_e\left(\frac{mg}{l}\right)}{m\ (g)} \times V\ (ml)$$

Where:
q_e = adsorption equilibrium in mg/g
C_o and C_e = initial and equilibrium concentration respectively (mg/l)
m = mass of adsorbent (g)
V = volume of aqueous solution (ml)

The adsorption efficiency for the different compounds was also calculated using the equation below:

$$\text{Percent removal (\%)} = \frac{C_o - C_e}{C_o} \times 100\%$$

Where C_o = initial concentration (mg/l)
C_e = concentration at equilibrium (mg/l)

The kinetics and thermodynamic studies were also carried out as have been previously described by Ifelebuegu et al. [17] and Ifelebuegu [9]. For the thermodynamic studies, the batch adsorption experiments were conducted at controlled temperatures of 15°C, 20°C, 25°C, 30°C ± 2.

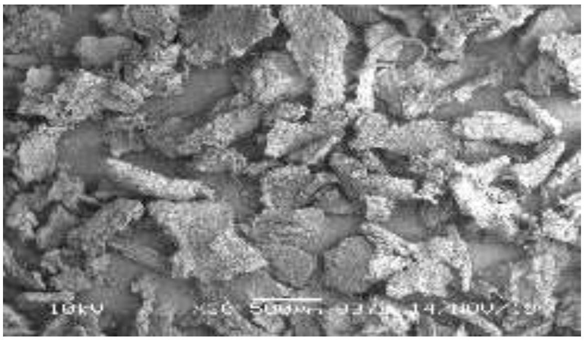
C. *Analytical Methods*

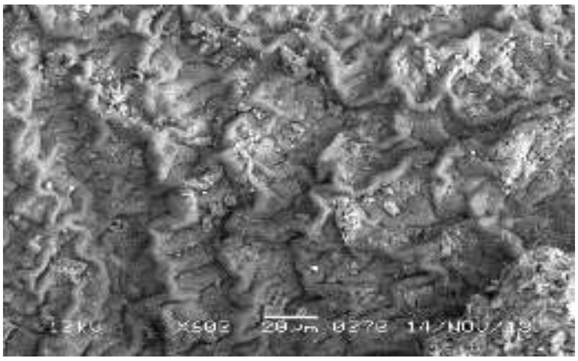
Samples were analysed using a high performance liquid chromatography (HPLC) fitted with a fluorescence detector. The HPLC system (Hewlett Packard Series 1050) consisted of Quaternary pump (model 79852A -United Kingdom), a 21 vial autosampler (model 79855A, Germany) and the data were analysed using Agilent ChemStation® software. Chromatographic separation was achieved using a C18 ODS-Hypersil analytical column (150 x 4.6mm, 5μm) maintained at 30°C temperature. Details of the analytical procedures have been previously described by Ifelebuegu et al. [5].

III. Results and Discussion

A. *Surface Characterisation*

The surface characteristics of tea leaves were investigated using Scanning Electron Microscope (SEM) (JSM-6060LV JEOL, Japan). The SEM images are shown in Figure 1a and b. The heterogenic nature of the pore surface of tea leaves is shown in the images. Tea leaves comprise of cellulose and lignin materials that could adsorb EDCs in aqueous medium [18, 19]. The surface morphology of tea leaves shows its porosity and rough surface with pores of different sizes which enhances the adsorption of organics [20].

a


b


Figures 1a and b: Scanning Electron Microscopy (SEM) images of blended Tea Leaves at different magnifications (a = x30, b = x600)

B. *Comparison of Tea Leaves with GAC*

The initial experiment was carried out to determine the equilibrium time for the removal of progesterone in wastewater and was compared with the performance of GAC. The results are expressed in Figure 2. It can be seen that adsorption reached equilibrium after about 60 minutes. TL showed a higher percentage removal of progesterone compared to GAC. The maximum adsorption capacity for tea leaves was 1.8 mg/g, while GAC has a maximum capacity of 1.4 mg/g. The enhanced performance of the tea leaves can be attributed to the presences of pores of various sizes and the rough surfaces of the tea leaves.

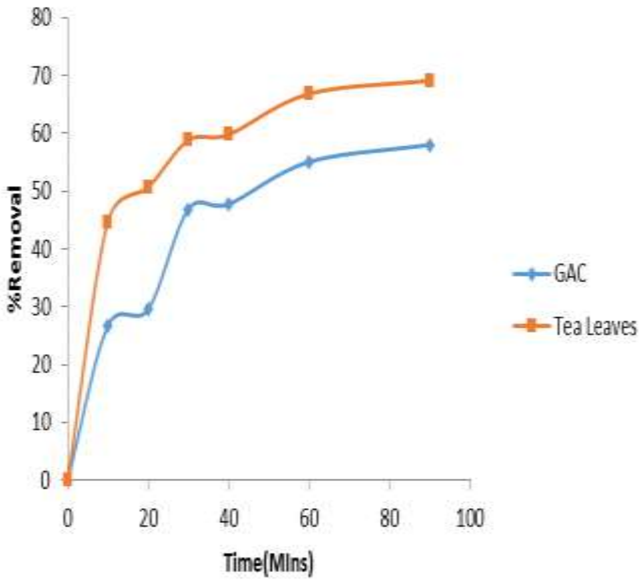


Figure 2: Plot of % removal of progesterone by tea leaves and GAC at pH 7, temperature 25°C

C. *Effects of pH*

Solution pH influences surface charge on the adsorbent particles as well as the potential ionisation of adsorbates [8, 21]. The effect of pH on the adsorptive removal of progesterone by waste tea leaves is shown in Figure 3. The percentage removal efficiency was highest at neutral pH. Similar results were obtained by Ifelebuegu et al.[17] for the adsorption of 17 β-estradiol and 17 α – ethinylestradiol by black tea leaves.

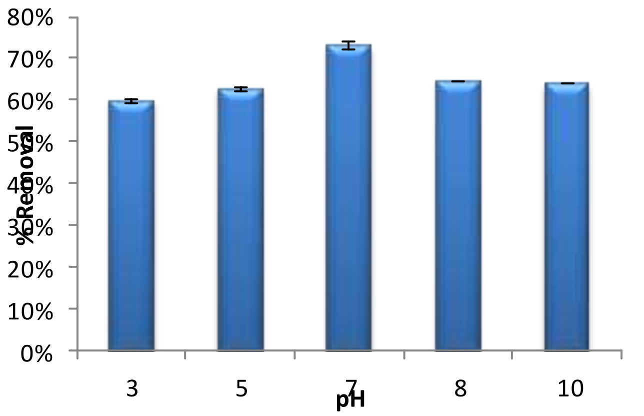


Figure 3: Percentage of progesterone adsorbed onto tea leaves at varying pH of wastewater and temperature of 25°C

D. *Intra-particle Diffusion Kinetics*

Intra-particle diffusion kinetic model was used to express the adsorption mechanism of progesterone onto the tea leaves as described by Ifelebuegu [9]. Linear graphs of q_t (mg/g) against the square root of the contact time, ($t^{1/2}$) (Figure 4) showed good fit ($R^2 = 0.9661$).

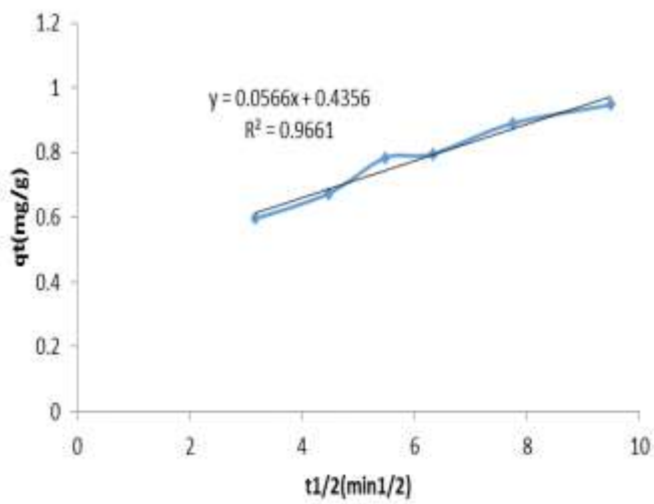


Figure 4: Intra-particle diffusion kinetic of Progesterone on tea leaves, pH 7, and temperature 25°C

The value of the intercept gives an idea of the boundary layer thickness. The value of the intercept in Figure 4 is low with K_p values of 0.0566 mg/g^{-1} min$^{-1/2}$. The plot did not pass through the origin, as can be seen, indicating some level of boundary layer control. Intra-particle diffusion does not contribute to the rate determining step but contributes to another process that may control adsorption. This suggests that adsorption is guided by the diffusion inside or within the pores of the adsorbents.

E. *Adsorption Thermodynamics*

Gibb's free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated as described in Ifelebuegu et al. [17] to evaluate the thermodynamic feasibility and thermal effects of the sorption processes. Table 1 shows the data obtained.

Table 1: Thermodynamic properties for progesterone adsorption on tea leaves and GAC at pH 7, Temperature 20°C to 35°C

Thermodynamic Parameter	Values
Gibb's Free Energy (KJ/mol)	-6.078
Enthalpy (KJ/mol)	-3.687
Entropy (J/mol K)	8.019

According to Soto *et al.*, [22], the values of (ΔG^o) are used to evaluate the driving force of adsorption, positive values of (ΔS^o) explain random arrangement of the adsorbate in the solid/solution interface while the values of enthalpy are the indication of the type of chemical reaction that occurs during the sorption process and the positive values suggest endothermic reaction while negative values indicate exothermic process. The negative values of ΔG^0 and ΔH^0 for progesterone adsorption onto tea leave suggest that the overall adsorption process is energetically favorable and spontaneous. The positive value of the entropy (ΔS^o) suggests the randomness of the solute and solution interface during the adsorption of progesterone molecules on the adsorbents [23]. The low value of entropy for the adsorption of progesterone onto tea leaves is attributed to a high amount of energy available for sorption. The ΔG^o value for tea leaves is less than 40kJ/mol. This is usually a characteristic of physical adsorption which is held by Van der Waal forces and is easily reversible in extreme conditions.

IV Conclusion

The use of waste tea leaves for the adsorptive removal of progesterone in wastewater was investigated in batch adsorption experiments. It was found to be effective and showed comparable adsorption capacity to GAC for the removal of progesterone. The maximum adsorption capacity of 1.8 mg/g was achieved at neutral pH for tea leaves compared to 1.4 mg/g for GAC. Intra-particle diffusion did not contribute to the rate determining step. The negative values of Gibb's free energy at – 6.0 KJ/mol and enthalpy at -3.7 KJ/mol, for tea leaves, indicated the feasibility, spontaneity and the physical nature of the adsorption of progesterone onto black tea leaves.

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