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Comparitive Studies for the Adsorption of Cadmium and Chromium from Aqueous Solution using Stalk of Solanum Melongena and Abelmoschus Esculentus

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Abstract: In this work, *Solanum melongena* stalk and *Abelmoschus esculentus* stalk which are agricultural by-products were used as adsorbent in the adsorption of heavy metals such as chromium and cadmium from aqueous solution. Various parameters such as biosorbent size, initial metal ion concentration, pH and contact time were performed to evaluate the adsorption process. *Solanum melongena* stalk and *Abelmoschus esculentus* stalk were collected, dried, powdered and sieved according to the sizes 50mm, 100mm and 150mm and then adsorption experiments were performed at 50 mg/L of initial metal ion concentration, pH range of 5.0 and time period until equilibrium constant is reached. Then finally the adsorption data were fitted to adsorption isotherms like Langmuir and Freundlich. It was found that the adsorption of chromium and cadmium by *Solanum melongena* stalk resulted in 91% and 98.88% of removal respectively. Similarly, it was found that the adsorption of chromium and cadmium by *Abelmoschus esculentus* stalk resulted in 98.74% and 99.98% of removal respectively. While comparing both, *Abelmoschus esculentus* stalk found to have greater efficiency. When *Abelmoschus esculentus* stalk is used as adsorbent, Freundlich isotherm was fitted for cadmium and chromium metal ions and when *Solanum melongena* stalk is used as adsorbent, Langmuir isotherm was fitted for cadmium and chromium metal ions.

Keywords: *Solanum melongena* stalk- *Abelmoschus esculentus* stalk- Initial metal ion concentration-pH-contact time -Freundlich isotherm- Langmuir isotherm.

Introduction

Pollution interacts naturally with biological systems. It is currently uncontrolled, seeping into any biological entity within the range of exposure. The most problematic contaminants include heavy metals, pesticides and other organic compounds which can be toxic to wildlife and humans in small concentration. There are existing methods for remediation, but they are expensive or ineffective. However, an extensive body of research has found that a wide variety of commonly discarded waste including egg shells, bones, peat, fungi, seaweed, yeast, vegetable stalks and carrot peels can efficiently remove toxic heavy metal ions from contaminated water. Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure. Though using biomass in environmental cleanup has been in practice for a while, scientists and engineers are hoping this phenomenon will provide an economical alternative for removing toxic heavy metals from industrial wastewater and aid in environmental remediation. Biosorption uses biomass raw materials which are either abundant (seaweeds) or wastes from other industrial operations (fermentation wastes). The metal-sorbing performance of certain types of biomass can be more or less selective for heavy metals. The concentration of a specific metal could be achieved either during the sorption uptake by manipulating the properties of a biosorbent, or upon desorption during the regeneration cycle of the biosorbent. Biosorption process of metal removal is capable of a performance comparable to its closest commercially used competitors, namely the ion exchange treatment.

Chromium is an industrial pollutant, which enters the ecosystem through soil, air and water and is an important heavy metal which is widely used in the metallurgies refractory, chemical and tannery industries. More than 17000 tons of chromium wastes are discharged to the environment annually as a consequence of industrial and manufacturing activitity[1]. Cadmium is a serious cause of environmental degradation[2]. Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seawood[3]. The removal of these highly toxic heavy metals can be performed by various biosorption techniques using naturally available biosorbents.

Bio-sorption is the best purification and adsorption technique. The search for new technologies involving the removal of toxic metals from waste water has directed attention to bio-sorption, based on metal binding capacities of various biological materials. Bio-sorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physic-chemical pathways of uptake algae, bacteria, fungi and yeasts have proved to be potential metal bio-sorbents[4].

Some types of biosorbents would be broad range, binding and collecting the majority of heavy metals with no specific activity, while others are specific for certain metals. Recent biosorption experiments have focused attention on waste materials, which are by-products or the waste materials from large-scale industrial operations. For e.g. the waste mycelia available from fermentation processes, olive mill solid residues[5], activated sludge from sewage treatment plants, biosolids[6] and aquatic macrophytes[7].

2. Materials and Methods

2.1 Biosorbent Preparation

Solanum melongena (Brinjal) and *Abelmoschus esculentus* (Lady's Finger) stalks were collected from vegetable market, at Coimbatore. The collected stalks were washed with distilled water. Then they were cut into small pieces and dried in hot air oven at 100˚C for 24 hours to remove moisture and to dry. The dried samples were ground and powdered. Then they were sieved and separated depending on mesh sizes 52mm, 72mm, 100mm, 150mm, 200mm and 240 mm respectively using the sieve shaker. The separated samples were weighed and sealed with zip-lock bags for the further analysis of adsorption studies.

2.2 Preparation of Synthetic Stock Solution

Chromium stock solution was prepared by dissolving 2.83g of Potassium dichromate (K2Cr2O7) in 1000ml of distilled water and 1ml contains 2.83mg of chromium. Similarly, Cadmium stock solution was prepared by 100mg of Cadmium nitrate ($Cd(NO_3)_2$) in 50ml of 10% HNO3 is made upto 1000ml in a volumetric flask with distilled water. 1ml contains 0.1mg of cadmium.

2.3 Experimental Procedure

2.3.1 Effect of Biosorbent Size

The experiments were conducted in 250ml conical flasks containing 100ml of 50mg/L metal (chromium/cadmium) solution and 1g of biosorbents at a constant agitation speed 150rpm. During the adsorption process, the flasks were agitated on a shaker until equilibrium is reached under room temperature. The size of biosorbent was varied at 50mm, 100mm and 150 mm. At the end of biosorption, the samples were filtered. The filtered solution was analyzed in Atomic Absorption Spectrophotometer to measure the heavy metal concentration present in that solution.

2.3.2 Effect of Heavy Metal Concentration

The experiments were conducted in 250ml conical flasks containing 100ml of 50mg/L metal (chromium/cadmium) solution and 1g of biosorbents at a constant agitation speed 150rpm. During the adsorption process, the flasks were agitated on a shaker until equilibrium is reached under room temperature.

The concentration of biosorbent was varied at 52mm, 72mm, 100mm, 150mm, 200mm and 240mm. At the end of biosorption, the samples were filtered. The filtered solution was analyzed in Atomic Absorption Spectrophotometer to measure the heavy metal concentration present in that solution.

2.3.3 Effect of pH

The experiments were conducted in 250ml conical flasks containing 100ml of 50mg/L metal (chromium/cadmium) solution and 1g of biosorbents at a constant agitation speed 150rpm. During the adsorption process, the flasks were agitated on a shaker until equilibrium is reached under room temperature. The pH was varied at 1, 2, 3, 4, 5, 6, 7, 8 and 9. At the end of biosorption, the samples were filtered. The filtered solution was analyzed in Atomic Absorption Spectrophotometer to measure the heavy metal concentration present in that solution.

2.3.4 Effect of Contact Time:

The experiments were conducted in 250ml conical flasks containing 100ml of heavy metal (chromium/cadmium) solution with optimum concentration at a constant agitation speed and constant dosage. During the adsorption process, the flasks were agitated on a shaker until equilibrium is reached under room temperature. Samples were withdrawn at regular intervals for every 30 minutes. At the end of biosorption, the samples were filtered. The filtered solution was analyzed in Atomic Absorption Spectrophotometer to measure the heavy metal concentration present in that solution.

3. Results and Discussion

3.1 Optimization of Parameters

Various parameters such as, initial metal ion concentration, biosorbent size, contact time and pH were optimized.

3.1.1 Effect of Biosorbent Size

Removal of chromium by *Abelmoschus esculentus* and *Solanum melongena* in the solution containing 50mg/L of initial metal ion was observed at the biosorbent size of 150mm as shown in Fig.1. Removal of cadmium by *Abelmoschus esculentus* and *Solanum melongena* in the solution containing 50mg/L of initial metal ion was observed at the biosorbent size of 150mm and 100mm respectively as shown in Fig.2.

3.1.2 Effect of Initial Metal Ion Concentration

Removal of chromium by *Abelmoschus esculentus* and *Solanum melongena* in the solution containing 50mg/L initial metal ion was observed to be 98.74% and 91% respectively. As the initial metal ion concentration increases, the percentage removal of chromium decreases as shown in Fig.3, because at lower concentration, the ratio of initial number of moles of metals ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of its minimum initial concentration[8]. As observed there is maximum removal of 98.74% of chromium in the solution containing 50mg/L initial metal ion of *Abelmoschus esculentus*.

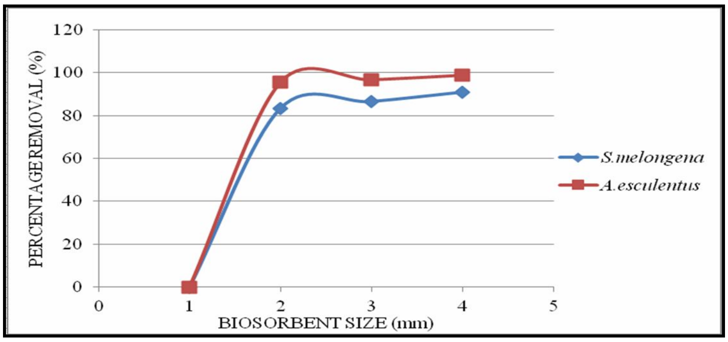

Fig.1. Effect of Biosorbent Size on % Removal of Chromium using *Solanum melongena* and *Abelmoschus esculentus* stalk

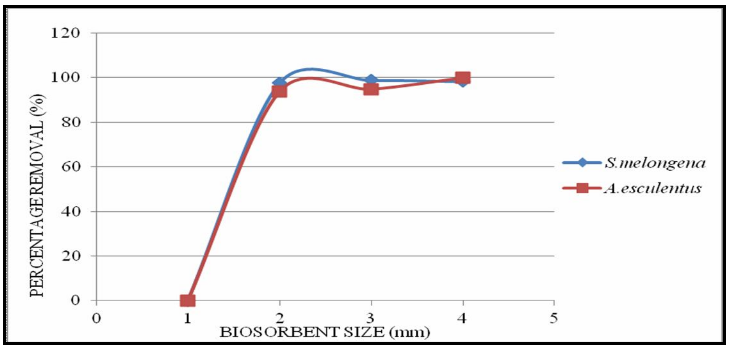

Fig.2. Effect of Biosorbent Size on % Removal of Cadmium using *Solanum melongena* and *Abelmoschus esculentus* stalk

Removal of cadmium by *Abelmoschus esculentus* and *Solanum melongena* in the solution containing 50mg/L initial metal ion was observed to be 99.98% and 98.88% respectively. As the initial metal ion concentration increases, the percentage removal of cadmium decreases as shown in Fig.4, because at lower concentration, the ratio of initial number of moles of metals ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of its minimum initial concentration[9]. As observed there is maximum removal of 99.98% of cadmium in the solution containing 50mg/L initial metal ion of *Abelmoschus esculentus*.

3.1.3 Effect of Contact Time

As the time increases the percentage removal increased till 98.74% for *Abelmoschus esculentus* and 91% for *Solanum melongena* in aqueous chromium solution as shown in Fig.5. Even though the contact time increased removal percentage remained constant since it attained equilibrium. As the time increases the percentage removal increased till 99.98% for *Abelmoschus esculentus* and 98.88% for *Solanum melongena* in aqueous cadmium solution as shown in Fig.6. Even though the contact time increased removal percentage remained constant since it attained equilibrium. During adsorption, metal ions are impregnated on the adsorbent surface until it is entirely covered with metal ions so the time increases as the percentage removal increases.

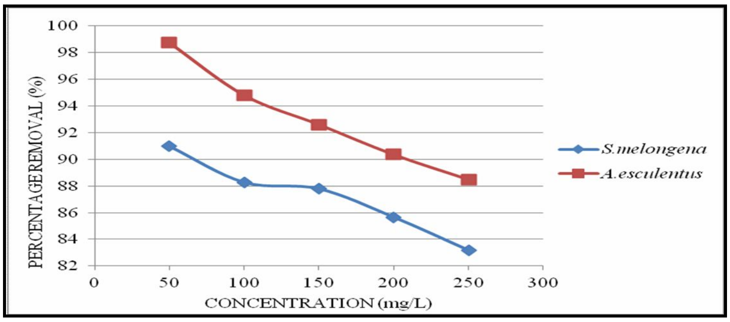

Fig.3. Effect of Initial Metal Ion Concentration for % Removal of Chromium using *Solanum melongena* and *Abelmoschus esculentus* stalk

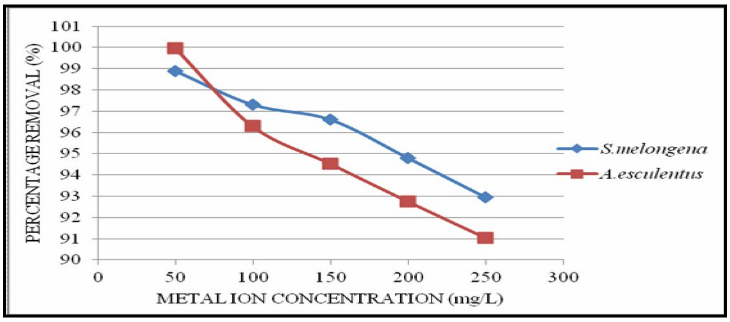

Fig.4. Effect of Initial Metal Ion Concentration for % Removal of Cadmium using *Solanum melongena* and *Abelmoschus esculentus* stalk

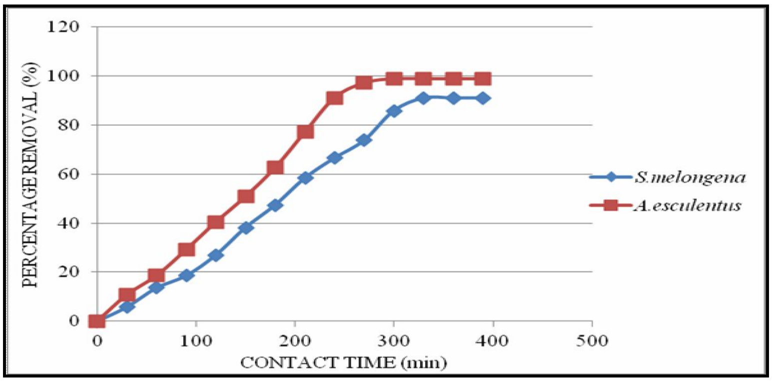

Fig.5. Effect of Contact Time on % Removal of Chromium using *Solanum melongena* and *Abelmoschus esculentus* stalk

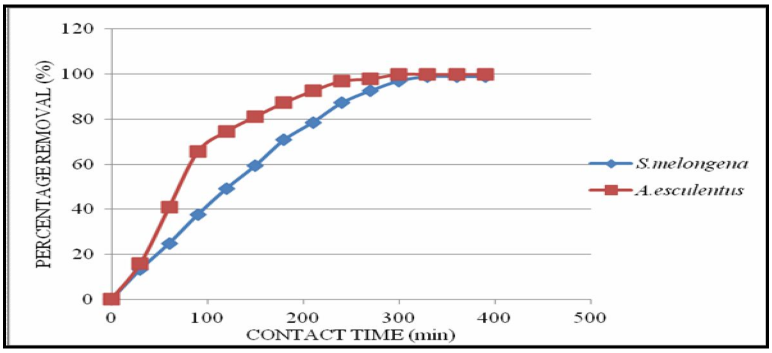

Fig.6. Effect of Contact Time on % Removal of Cadmium using *Solanum melongena* and *Abelmoschus esculentus* stalk

3.1.4 Effect of pH

The percentage removal of chromium increase with increase in pH 4.0 to 5.0 and decreases with further increase in pH as shown in Fig.7. Maximum sorption of 98.74% in *Abelmoschus esculentus* and 91% in *Solanum melongena* of chromium occurs at pH 5.0. The percentage removal of cadmium increase with increase in pH 4.0 to 5.0 and decreases with further increase in pH as shown in Fig.8. Maximum sorption of 99.98% in *Abelmoschus esculentus* and 98.88% in *Solanum melongena* of cadmium occurs at pH 5.0. This is probably due to the protonation of the adsorbent surface and pH increase promotes competition between OH^- and metal species[10].

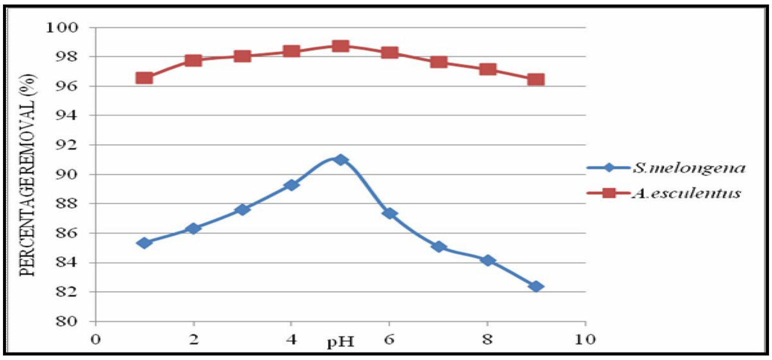

Fig.7. Effect of pH on adsorption of chromium using *Solanum melongena* and *Abelmoschus esculentus* stalk

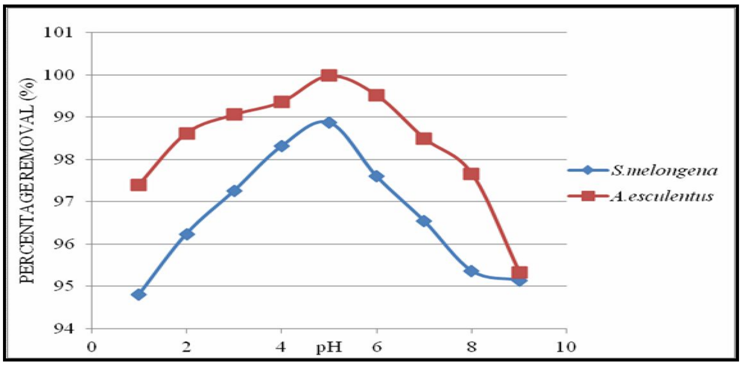

Fig.8. Effect of pH on adsorption of cadmium using *Solanum melongena* and *Abelmoschus esculentus* stalk

3.5. Equilibrium models for the biosorption of chromium

Adsorption isotherms show the relation between the amounts of metal adsorbed per unit weight of adsorbate remaining in a test medium at equilibrium. The capacity of *Abelmoschus esculentus* and *Solanum melongena* to remove chromium and cadmium was evaluated using Langmuir and Freundlich isotherm equations.

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by

$$\frac{1}{q_{eq}} = \frac{1}{Q_{max} \cdot b} + \frac{1}{c_{eq}}$$

where, q_{eq} is the amount adsorbed at equilibrium (mg/g), c_{eq} is the equilibrium concentration of metal ions in solution (mg/L) and b is a constant related to the energy of adsorption. Fig.9 depicts the Langmuir Isotherm plot for chromium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk and Fig.10 depicts the Langmuir Isotherm plot for cadmium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk.

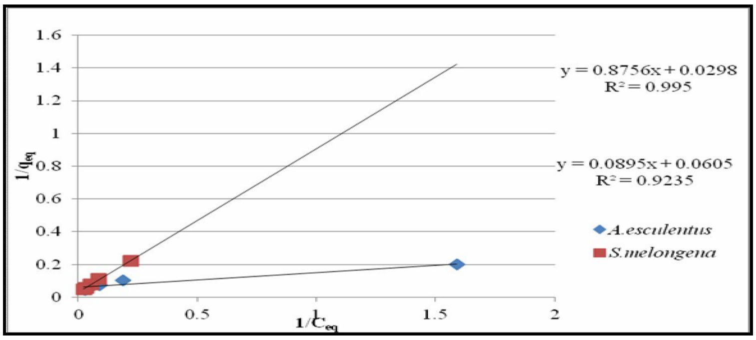

Fig.9. Langmuir Isotherm plot for chromium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk

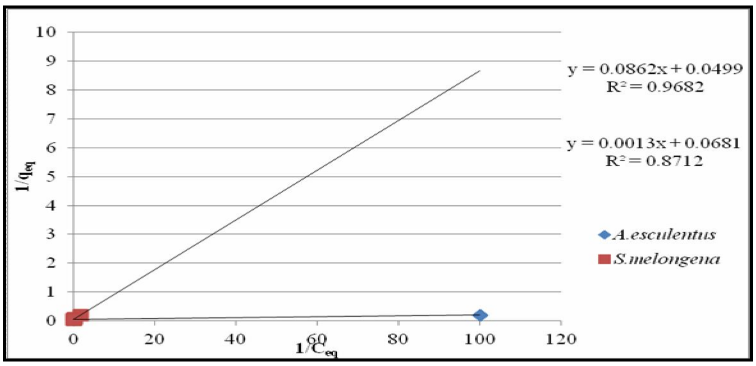

Fig.10. Langmuir Isotherm plot for cadmium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk

Table.1. Langmuir isotherm constants for the chromium and cadmium ions adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk

Adsorption Isotherm Parameters for Chromium					
Sample	**Slope**	**Intercept**	**Q_{max} (mg/g)**	**b (L/mg)**	**R^2**
Solanum melongena	0.8756	0.0298	33.56	0.034	0.995
Abelmoschus esculentus	0.0895	0.0605	16.53	0.68	0.9235
Adsorption Isotherm Parameters for Cadmium					
Sample	**Slope**	**Intercept**	**Q_{max} (mg/g)**	**b (L/mg)**	**R^2**
Solanum melongena	0.0863	0.0499	20.04	0.578	0.9681
Abelmoschus esculentus	0.0013	0.0681	14.68	52.63	0.8712

Table.2. Parameters Used to Relate Separation Factor with the Type of Adsorption

R_L Value	**Type of Fit**	**Estimated R_L**
$R_L > 1$	Unfavourable	-
$R_L = 1$	Linear	-
$0 < R_L < 1$	Favourable	0.2
$R_L = 0$	Irreversible	-

The Freundlich model is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by

$$\ln q_{eq} = \ln k_f + \frac{1}{n} \ln c_{eq}$$

where, q_{eq} is the amount adsorbed at equilibrium (mg/g), c_{eq} is the equilibrium concentration of metal ions in solution (mg/L), n is indicative of bond energies between metal ion and the adsorbent and k is related to bond strength. Fig.11 depicts the Langmuir Isotherm plot for chromium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk and Fig.12 depicts the Langmuir Isotherm plot for cadmium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk.

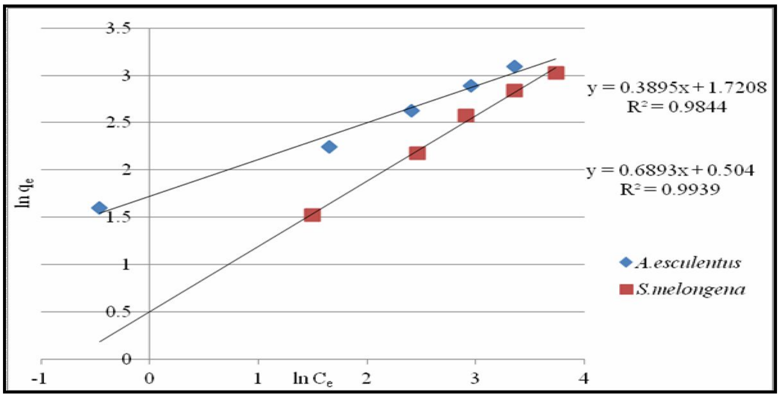

Fig.11. Freundlich Isotherm plot for cadmium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk

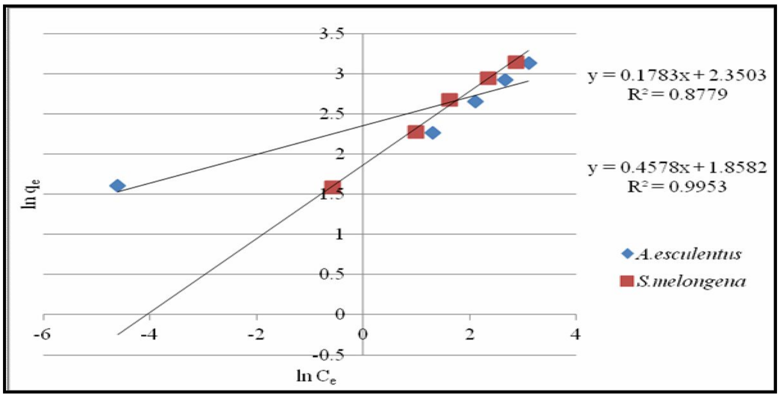

Fig.12. FreundlichIsotherm plot for cadmium adsorption into *Solanum melongena* and *Abelmoschus esculentus* stalk

4. Conclusion

The presence of heavy metals in Industrial effluents is extremely undesirable, as they eventually seem to affect living organisms due to prolonged exposures which seem to be highly toxic and dangerous. Since pollution is a major concern, development of cheaper, efficient biomass sources obtained for many industries as wastes can be used as biosorbents was initiated. Here the use of these biosorbents through the process of adsorption has served the needs of many industries and is also highly efficient, economic and very easier method for effluent treatment processes.

The present study evaluates the properties of two different biosorbents, *Abelmoschus esculentus* stalks and *Solanum melongena* stalks. Aqueous solution of chrome-plating industry was collected and checked for the presence of metals, chromium (Cr) and cadmium (Cd). The adsorption process which is a function of adsorbent is based on the adsorbent size, metal ion concentration, pH and contact time and analysis were performed by Atomic Absorption Spectrophotometer (AAS). The efficiency of heavy metal removal after treatment in aqueous waters are determined to be 91% and 98.32% for chromium and cadmium respectively in the case of *Solanum melongena* stalk and 98.74% and 99.98% for chromium and cadmium respectively in the case of *Abelmoschus esculentus* stalk.

From the analysis it was found that bio-sorbent, *Abelmoschus esculentus* stalk is very effective enough than *Solanum melongena* stalk and promising in serving as cheap and readily available biosorbents for treatment of aqueous solution and in turn can also minimize the risks of heavy metal contaminations in industrial waste water providing a clean earth for an healthier and better living.

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