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Research Article

Removal of Heavy Metals by Low Cost Material.

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ABSTRACT

In the Present work the enicostemma littorale are used as adsorbent for removal of heavy metals like Fe(III), Cu(II), Cr(II) from aqueous solution. The adsorption characteristics of all three metals on enicostemma littorale were evaluated as a function of varying adsorbent dose, temperature and time. The percentage removal of Fe(III), Cu(II), Cr(II) by titanium oxide enicostemma littorale carried under different conditions, during this findings was significant. The order of adsorption on titanium oxide enicostemma littorale of metals ions were Cu >Fe>Cr during the findings. The adsorption data fitted well into Freundlich and Langmuir adsorption models. The results show that titanium oxide enicostemma littorale hold a great potential in removal of metal ions from aqueous solution. The thermodynamic study has showed that the Fe(III), Cu(II), Cr(II) ions adsorption on the surface of titanium oxide enicostemma littorale was physical adsorption and the process was spontaneous and exothermic.

KEYWORD

Enicostemma littorale, Heavy metal ions, Freundlich isotherm, Langmuir isotherm, Low cost material

1. INTRODUCTION

Heavy metals such as Iron, Copper, Lead, Zinc, Nickel, and Chromium have harmful effects on human physiology and other biological system s when they exceed the tolerance level [1]. They pose serious health hazards through entry into the food chain; therefore they must be removed from industrial waste effluents. In recent past development of efficient and eco-friendly methods for removal of heavy metals are receiving attention by agro waste as adsorbent by various researchers[2]. To date researches suggest that man y of the issues involving water quality could be resolved using enicostemma littorale resulting from the development of nanotechnology. Recently enicostemma littorale are being used in adsorption processes for water purification [3-4]. In the present investigation an attempt has been made t o study the feasibility and efficiency of enicostemma littorale for the adsorption of Iron, Copper and Chromium. The adsorption of heavy metals ions from aqueous solution was carried to study varying adsorbent dose, temperature & time.

Enicostemma littorale is traditionally used in India as a stomachic, bitter tonic, carminative to reduce fever. As a tonic for appetite loss. In Indian Ayurveda medicine, E. littorale is taken in combination with other herbs, especially for diabetes. E. littorale is administered in Ayurvedic pill form for treating type 2 diabetes since it plays a major role in reducing blood glucose and increases serum insulin level and significantly improves kidney function, lipid profile, systolic and diastolic blood pressure and pulse rate. E. littorale has demonstrated its anti-inflammatory activity and tumor inhibition in rats. The plant possesses a sec. compound namely swertiamarin which shows central nervous system (CNS) depressant effects in rats. Nampalliwar and Godatwar observed that E. littorale enhances glucose dependent insulin release. The hot aqueous extract of E. littorale has also been used by the traditional herbs for the treatment of dyspepsia and malaria. E. littorale showed a prominent antibacterial activity against *satphycoccus aureus, Pseudomonas auguginosa, Salmonella typhi, Shigella sonnei* and antifungal activity against *Aeromonas hydrophila, C. albicans.*

Botanical Name: Enicostemma axillare (LAM) RAYNAL
Habit: Herb Hindi vernacular name- chhotachirayata, nawarinahli
Class: Dicotyledon
Subclass: Gamopetalae
Series: Bicarpellatae
Order: Gentialatae
Family: Gentianaceae
Genus: Enicostemma
Species: axillare

2. MATERIALS AND METHODS

2.1. Adsorbent

The adsorbent s elected for the present work was enicostemma littorale. The 99.9% pure form of titanium oxide enicostemma littorale (TON) made available from MK nano Sales of MK Impex Corp. Canada of desired particle size (30-50nm). This adsorbent been used throughout the experimental work. The particle size of adsorbent selected for these experiments were on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid.

2.2. Preparation of Adsorbate Solution

Iron, Copper and Chromium were the metal ions selected for the present investigation. The chemicals were all of Analytical grade and used without further purification. The solutions were prepared in doubly distilled water. Prepared by using first metal distillation unit and then all quick fit glass assembly in permanganate conditions, wherever necessary the prepared solutions were standardized as per literature[5].

2.3. Batch Adsorption Experiments

Each batch adsorption study was carried out by contacting TON with the ions Fe(III), Cu(II), Cr(II) under different conditions for 60 minutes in glass tube. The uptake of metal study on TON was carried systematically and at temperature 30^{o}C to evaluate effect of adsorbent dose, contact time on adsorption of metal ions. The effect of temperature on the adsorption was carried out in order to study the thermodynamics of the process. Each study was conducted in thermo stated water bath and the residual metal ions were analyzed. The amount of metal ions adsorbed from solution was determined by difference [5].The concentration of metal ion solution were determined from calibration curve spectrophotometrically (shimatzu-12 11) at their respective wave lengths. i.e. λ max. system is more ordered) and this order may be lost when the ions are adsorbed on the surface due to release of solvated water molecules.

Table 1. Thermodynamic parameters at different temperature.

Adsorbate	**Temperature**	**- G/KJ**	**- H/KJ**	**S/J**
Iron	303	3.50	8.825	28.02
	308	1.888		
	313	3.100		
Copper	303	2.792	7.392	23.44
	308	2.0901		
	313	6.912		
	303	6.503		

Chromium			3.774	10.20
	308	6.222		
	313	6.0912		

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature

The magnitude of the temperature effects for the adsorption process is one of the most important criteria for the efficient removal of heavy metals from the waste water [6].

The data of heavy metal ions adsorption on to TON at different temperature indicates decrease in adsorption with rise in temperature [7] from 308K to 318. These effects may attributes to a negative temperature co-efficient of solubility of the solute or to a steep simultaneous decrease of real adsorption of solvent.

3.2. Effect of Contact Time

In adsorption studies, effect of contact time plays vital role irrespective of the other experimental parameters affecting adsorption kinetics and dynamics. The adsorption studies were carried out at different contact time at constant initial concentration of Iron, Copper and

Chromium with fixed dose of adsorbent. In the present investigation it is observed that at initial stage adsorption is rapid and become slow and get stagnated with increase in time. This may be due to immediate solute adsorption on the surface of adsorbent with subsequent slow removal of the remaining amount of metal ions. Similar findings are also reported by other researchers [8].

3.3. Effect of Adsorption dose

Effect of adsorption dose plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. The present study reveals that as the adsorbent dose increase from 1 gm to 5 gm, the removal efficiency of all free metal ions increase on the surface of TON. The increase in adsorption with increase in TON dose may be attributed to the increase in the availability of active sites or surface area at higher concentration of the adsorbent.

3.4. Adsorption Isotherms

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution[9].The adsorption data for a wide range of adsorbate concentration and adsorbent doses were analysed using Langmuir and Freundlich isotherm in order t o find the adsorption capacity of TON adsorbate. Freundlich theory suggested that the ratios of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solutions are not constant at different concentration of solution[10].The Freundlich isotherm was verified by using least square fit and regression analysis and computer programming in EXCEL. The value of regression coefficient r^2 found to be very close to one which indicates the good correlation exists between log X/m and log c. The Langmuir mode[11] represents monolayer adsorption on a set of distinct localized adsorption sites having the same adsorption energies. The essential characteristics of Langmuir isotherm is

expressed in terms of dimensionless constant separation factor or equilibrium factor R_L which is indicative of the isotherm and is indicative of the nature of the isotherm and is enlisted below as:

R_L value	**Types of Isotherm**
$R_L > 1$	**Unfavorable**
$R_L = 1$	**Linear**
$0 < R_L < 1$	**Favorable**
R = 0	**Irreversible**

The adsorption of all three metal ions are favorable on to the surface TON as R_L value in the present study falls in the $O < R_L < 1$.

3.5. Thermodynamic parameter

The adsorption of all three metal ions are favorable on to the surface TON as R_L value in the present study falls in the $O < R_L < 1$.

Thermodynamic parameters evaluate the nature of adsorption of adsorbate and its magnitude during adsorption process. The change in Gibbs free energy ($\triangle$ G), enthalpy changes ($\triangle$ H) and entropy change ($\triangle$ S) were calculated and are summarized in the tabular form. According to Laura[12] $\triangle$ G upto -15 KJ/ mole are connected with physical interaction between adsorption site and metal ions is physical adsorption. In the present investigation $\triangle$ G values of Fe (III), Cu (II), and Cr (II) are below -15 KJ/mole indicates physical adsorption. The negative value of $\triangle$ H indicates exothermic process. The positive value of $\triangle$ S suggest increased randomness at the solid-liquid interface solvent molecule which are displayed by the adsorbed species gain more translational entropy than was lost by the adsorbate ions Furthermore before adsorption process takes place the adsorbate ions are heavily solvated.

4. CONCLUSION

It has been proved that activated TON is an excellent adsorbent for removal of heavy metal ions from aqueous solution under certain physiochemical conditions. The result indicates the potentially practical value of TON as adsorbent. The dimensionless equilibrium parameter R_L found to be in the range between 0 to 1 is indicative of favorable adsorption onto the surface of thermodynamic parameters $\triangle$ G, $\triangle$ H and $\triangle$ S shows spontaneous process.

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