Lemongrass Powder used an Adsorbent for Treatment of Chromium from Tannary Waste Water

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Abstract: In the present work was represent the lemon grass powder preparation and prepared power was used for adsorbent to removal of Hexavalent Cr present in tannery water by adsorption phenomena. The collected plant material was allowed to dry in sunshade for a week and after that it was crushed, powdered and homogenizing. The homogenized powder is used as adsorbent in the present study. Although evaluate the performance of adsorption activity of prepared lemon powder However in this work also focus on the concentration of adsorbate .effect of pH and effect of surfactant data are determined used to kinetics and isotherm methods. The homogenized powder is used as adsorbent in the present study. The colorimetric method is useful for the determination of hexavalent chromium in water in the range from 0.1 to 1 ppm. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell paths. The hexavalent chromium is determined colorimetrically by reaction with 1,5diphenylcarbazide in acid solution. The removal of chromium in aqueous solution by using adsorption technology was studied by batch adsorption process.

Keywords: Lemon grass powder, Chromium, ternary waste.

1. Introduction

Water resources are important to natural ecosystem and human developments. Water supports all forms of life on earth. The availability of clean water to the human population is of paramount importance. Water pollution has been defined as any human-caused contamination of water that reduces its usefulness to humans and other organisms in nature (USEPA-905-F-97-011, 1997). Most of the pollution of water supplies comes from anthropogenic sources which include contaminants such as herbicides, pesticides, fertilizers, hazardous industrial chemicals, detergents, pathogens, heavy metals, organic solvents and textile dyes that find their way into water supplies. In recent years, heavy metal contamination in ground water has been found to be alarming in Asian countries like Bangladesh, India and China ¹-⁴. Specific rocks types, geochemical conditions, proximity to hydrologic and landscape variables are found to be the reasons of higher content of heavy metals in ground

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Heavy metals are conventionally defined as elements with metallic properties and have an atomic number greater than 20. Pb, Cd, Zn, Cu and Hg can be given as the examples of heavy metals. Some of these metals are micronutrients necessary for plant growth such as Zn, Cu, Mn, Ni and Co while others have unknown biological functions such as Cd, Pb and Hg\(^8,9\). Some heavy metals like Cu, Zn, Se, Fe and Ni are essential elements which are required for maintaining the metabolism of all living organisms. They are used as co-factors for enzymes or proteins but they are needed in very small amounts. Metals like Cd, Hg and Pb are non-essential metals. Based on their concentration, not only the essential but also the non-essential metals play a key role as cell toxins. This phenomenon comes from the unspecific binding of the metals to important biomolecules and proceeds with blocking of functional groups, displacement of essential elements, the change of active conformation of the biomolecule. Hence, heavy metals can have toxicological effects on human body. A number of techniques are available for the removal of inorganic pollutants (heavy metals) from industrial waste water. The removal of heavy metals from water (drinking) can be achieved through precipitation, flocculation, solvent extraction, ion exchange, reverse osmosis\(^10-12\).

The process of adsorption has now become one of the preferred methods for the removal of toxic contaminants from water as it has been found to be effective, economical, versatile and relatively simple\(^13-18\). Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse of adsorbents and low capital cost. The adsorption process has acquired global importance for reducing the problem of contamination of water and air. The process has become a significant addition to Green Chemistry endeavors. In this paper represent the preparation of lemon grass powder adsorbent and it is used for the absorption to the removal of hexavalent chromium present in the ternary waste water.

2. Experimental Work

2.1 Collection of wastewater sample for cr(vi) removal

Waste water sample were collected from leather industry in chrompet, Chennai City

2.2 Preparation of adsorbate (lemon grass powder) stock solution and working solution

All the experiment working solutions were prepared by diluting the stock solution with distilled water.

2.3 Preparation of adsorbent

The plant Lemongrass (Cymbopogom citratus) was collected from Chitannavessel rock near Pudukottai, Tamilnadu and identified by the botanist of Sri Sairam Siddha Medical College, Tamaram, Chennai and a specimen was kept in their laboratory.

The collected plant material was allowed to dry in sunshade for a week and after that it was crushed and powdered. and then screened for homogenizing. The homogenized powder is used as adsorbent in the present study

2.4 Colorimetric method for determination of hexavalent chromium in water

The colorimetric method is useful for the determination of hexavalent chromium in water in the range from 0.1 to 1 ppm. This range can be extended by appropriate sample dilution or concentration and/or use of longer cell paths. The hexavalent chromium is determined colorimetrically by reaction with 1,5 diphenylcarbazide in acid solution [Fig 1].
Fig.1, 5-diphenyl carbazole

A red-violet colored complex of unknown composition is produced. The reaction is very sensitive, the molar absorptivity based on chromium, at 540 nm.

\[
2\text{CrO}_4^{2-} + 3\text{C}_{13}\text{H}_{12}\text{N}_{4}\text{O} + 8\text{H}^+ \rightarrow [\text{Cr}^{3+}(\text{C}_{13}\text{H}_{12}\text{N}_{4}\text{O})_{2}]^+ 
\]

When DPC added to chromate ion in the presence of sulphuric acid, a chromium DPCA complex is formed, which shows absorption at 540 nm.

2.5 Experimental procedure

2.5.1. Estimation of chromium(vi) in the sample:

Exactly 1 g of potassium dichromate was weighed and dissolved in 1000 ml of distilled water. This is known as stock solution, each ml of which contains one mg of potassium dichromate. From the stock solution 10 ml was pipette out in a 100 ml standard measuring flask and made up in to 100 ml using distilled water. It is called as 100 ppm solution. Similarly 200, 300, 400 and 500 ppm solutions were prepared used required stock solution. Calorimeter was calibrated to optical density (OD) 0.00 using distilled water at 560 nm and made ready to measure OD of the samples. Although 20 ml of sample having 100 ppm potassium dichromate was pipette out in a colorimetric jar and 1 ml of 1,5 – diphenylcarbazide (100 mg in 100 ml of alcohol) was added to it. The addition of 1 ml of concentrated Sulphuric acid was added a pink colour of afterthat complex was formed. From this 10 ml was taken in a cuvette and its OD at 560 nm was recorded. Similarly OD values for all the samples (200, 300, 400 and 500 ppm) were recorded and tabulated (table 5.1) the table 5.1 values are shown that test sample whose Cr content was to be removed was also subjected to the same treatment as explained above and its OD was recorded.

2.5.2 Adsorption equilibrium experiment

The batch adsorption experiment was carried out the to determine the equilibrium time. 100 ml of sample solution was added to one gram of adsorbent and allowed to agitate in a shaker at 200 rpm. at 27°C. After 10 minutes of agitation, the content of the flask was filtered and from the filtrate 10 ml was measured in a colorimetric jar and 1 ml of 1,5 – diphenylcarbazide (100 mg in 100 ml of alcohol) was added above sample solution. This was followed with addition of 1 ml of concentrated Sulphuric acid. a pink colour complex was formed. From this 10 ml was taken in a cuvette and its OD at 560 nm was recorded. The remaining 90 ml of the sample was again added to one gram and the procedure was repeated. This step was continued until same OD was obtained. The values are recorded and given in table 1.1. The concurrency of OD shows the time required for the attainment of equilibrium.

To study the various factors influencing the adsorption process such as effect of adsorbent dose, concentration of adsorbate, contact time, PH and Surfactant the following experiments were carried out and the readings are discussed and tabulated.
3. Results and Discussion

3.1 Colorimetric estimation of chromium(vi) in the sample:

In this experiment stock solution 10 ml was pipetted out into a 100 ml standard measuring flask and made up in to 100 ml used distilled water. It is called 100 ppm solution. Similarly 200, 300, 400 and 500 ppm solutions were prepared using required stock solution. A OD of the pink colour complex formed by addition of 1,5-diphenyl carbazide and conc Sulphuric acid with 100 200,300,400 and 500 ppm were recorded and tabulated. The OD of test sample was also recorded and tabulated.

Table 3.1 calibration method

| S.No | Concentration of potassium dichromate (ppm) | Optical density |
|------|---------------------------------------------|----------------|
| 1    | 10                                          | 0.31           |
| 2    | 20                                          | 0.41           |
| 3    | 30                                          | 0.56           |
| 4    | 40                                          | 0.78           |
| 5    | Test sample                                 | 0.96           |

Using the above values a calibration curve was drawn from which the slope of the trend line was observed. (Fig 3.2). The best fit for the above data was found from the trend line which is

\[ y = 0.0156x + 0.125 \].

Substituting \( y = 0.96 \) we get \( x = 7.052 \) ppm

From stoichiometry 294 g of \( K_2Cr_2O_7 \) (2(39) + 2(52) + 7(16)) contains 104 (2(52)) g of Cr

Therefore \( 7.052 \) mg of \( K_2Cr_2O_7 \) contains \( \frac{104 \times 7.052}{294} \)

\( =2.494 \) mg of Cr
3.2 Batch adsorption process

The batch adsorption experiments were conducted in 250ml conical flask containing adsorbent and 50 mL of sample solution at a pH of 2.2. The flasks were agitated in a shaker at 200 rpm. and 27°C until the equilibrium was reached. After decantation and filtration, the OD were measured at 560 nm using colorimeter.

The agitation was carried out for 10, 20, 30, 40, minutes. Each time after decantation and filtration OD was found out The constant values at 50 min and 60 min shows the attainment of equilibrium.

Table – 3.2 Batch adsorption process

| S.No | Time | Optical density |
|------|------|-----------------|
| 1    | 10   | 0.50            |
| 2    | 20   | 0.44            |
| 3    | 30   | 0.35            |
| 4    | 40   | 0.35            |

3.3 Effect of adsorbent dose

In order to study the effect of adsorbent mass on the adsorption of Chromium, a series of adsorption experiments was done with different adsorbent dosages at initial concentration of 10g. Figure 5.2 shows the effect of adsorbent dose on the removal of Chromium.

As the adsorbent dosage increases from 10 – 40 g, the percentage of Chromium adsorbed get increased from 4 - 51 % .This shows that when dose of adsorbent increases, the percentage of Chromium removal increases’. This suggests that for better removal of Chromium the adsorbent dosage should be as high as possible. The increase in adsorption may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents. However, no significant changes in removal efficiency were observed beyond 50 mg adsorbent dose. Due to concentration of adsorbent particles, there is no increase in effective surface area of adsorbent.

OD Before Adsorption : 0.96 Quantity of adsorbent : various grams
Time : 40 min Concentration of adsorbate : 25 ml

Table – 3.3 Effect of adsorbent dose on adsorption

| S.No | Weight of Adsorbent (gm) | Optical Density | % removal = \( \frac{A_0 - A_1}{A_0} \times 100 \) |
|------|--------------------------|----------------|-----------------|
| 1    | 1                        | 1.22           | 27              |
| 2    | 2                        | 1.48           | 54              |
| 3    | 3                        | 1.69           | 76              |
| 4    | 4                        | 2.00           | 108             |
The above graph shows that when the concentration of adsorbent increases the percentage of Chromium removal increases. From this it is clear that the adsorption of is effective only at high concentration of adsorbent.

3.4 Effect of concentration of adsorbate (chromium in tannery waste water)

Exactly one gram of adsorbent (lemon cross powder) was weighed and adsorbate (chromium in tannery waste water) of various volume is added to it and allowed to be shaken for 40 mints in orbital shaker with 200 rpm. The optical density of the adsorbate at 660 nm after one hour was observed and the result in the following Table 5.4.

Table.3.4 Effect of concentration of adsorbent on adsorption

| S. No | Concentration of adsorbate (ml) | OD After Adsorption | % removal = \( \frac{A_0 - A_1}{A_0} \times 100 \) |
|-------|-------------------------------|---------------------|-----------------------------------------------|
| 1     | 10                            | 0.6                 | 52.5                                          |
| 2     | 20                            | 0.53                | 72.5                                          |
| 3     | 30                            | 0.45                | 95.3                                          |
| 4     | 40                            | 0.36                | 106.1                                          |
The above graph reveals that when the concentration of adsorbate (chromium in tannery waste water) increases the adsorption decreases.

3.5 Effect of contact time

Exactly one gram of adsorbent was weighed and 50 ml adsorbate (chromium in tannery waste water) was added to it and allowed to be shaken for 60 mints in orbital shaker with 200 rpm. The optical density of the adsorbate (chromium in tannery waste water) at 660 nm after different contact time was observed and shown in Table 3.5.

The chromium removal increased with the increase of contact time initially, and no much change was observed after the equilibrium was reached as shown in Fig 3.5. The change in the rate of adsorption might be due to the fact that initially all the adsorbent sites would have been vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and metal concentrations.

OD Before Adsorption : 0.96 Concentration of adsorbate : 25 ml
Time : 40 min Concentration of adsorbent : 1g

Table – 3.5 Effect of contact time on adsorption

| S.No | Contact time(minutes) | Optical density | \% removal = \frac{A_0 - A_1}{A_0} \times 100 |
|------|----------------------|-----------------|-----------------------------------|
| 1    | 30                   | 0.52            | 40.00                             |
| 2    | 60                   | 0.30            | 68.75                             |
| 3    | 90                   | 0.25            | 73.95                             |
| 4    | 120                  | 0.14            | 85.41                             |
The above graph shows that the percentage removal increase with increases in contact time and this confirms that the rate of adsorption process is very high at longer period.

3.6 Effect of pH

Exactly 10 gram of adsorbent was weighed and 50ml of adsorbate(chromium in tannery waste water) was added to it and, various volume of HCl also added. The mixture was allowed to be shaken for 30 mins in orbital shaker with 200 rpm. The optical density of the adsorbate (chromium in tannery waste water) at 660 nm after one hour was observed and recorded shown in table 3.6.

Table 5.6 Effect of pH on adsorption

| S.No | Volume of HCl(ml) | pH  | Optical Density | % removal= \( \frac{A_0 - A_1}{A_0} \times 100 \) |
|------|------------------|-----|-----------------|-----------------------------------------------|
| 1    | 0.5              | 0.301| 0.85            | 11.45                                         |
| 2    | 0.1              | 1.00 | 0.72            | 40                                            |
| 3    | 0.05             | 1.301| 0.35            | 63                                            |
| 4    | 0.01             | 2.00 | 1.05            | 9.3                                           |
The above graph shows that at low pH, the percentage removal very low. At particular pH , the percentage removal is maximum and this shows that adsorption is effective at pH less than 0.5. Shown in Figure-3.6 a consistent increase in adsorption capacity was noticed as the pH increased from 0.3 – 1.3, whereas in the range 1.5 – 2.5, the adsorption amount was only slightly affected by pH. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged cations due to electrostatic repulsion. In addition, lower adsorption at acidic pH might be due to the presence of excess H+ ions competing with cations for the available adsorption sites.

3.7 Effect of surfactants

Exactly 10 gram of adsorbent was weighted, 50 ml of adsorbate(chromium in tannery waste water) and various volumes surfactant sodium dodecyl sulphate (SDS) are added to it and allowed to be shaken for 60 mins in orbital shaker with 200 rpm. The optical density of the adsorbate at 660 nm after one hour was observed and shown in table 3.7.

OD Before Adsorption \( (A_0) \) : 0.96

Concentration of adsorbent : 1 gm

Time : 40 mts

Concentration of adsorbate : 25 ml

Table.3.7 Effect of surfactants on adsorption

| s.n o | Surfactant (ml) | Optical density | % removal | A_0-A_1 | 100 |
|-------|-----------------|-----------------|-----------|---------|-----|
| 1     | 10              | 2               | 108       |         |     |
| 2     | 20              | 1.72            | 76.16     |         |     |
| 3     | 30              | 1.50            | 56.25     |         |     |
| 4     | 40              | 1.41            | 46.87     |         |     |
The above graph shows that the percentage removal decreases with the increase of concentration of surfactant sodium dodecyl sulfate (SDS). This may be attributed due to tendency of surfactant to increase surface tension between the liquid layer and the solid layer of adsorbent. From this it is clear that increase of surfactant decreases the efficiency of adsorption.

4. Conclusion

Chromium present in the industrial effluent enters in to the surface water, ground water and also sewage water. Higher concentration in water can alter the aesthetic quality of water. Hence its presence in aquatic environment must be checked regularly. The chromium removal process which is outlined in this work can be utilized well in any water treatment process. The removal of chromium in aqueous solution by using adsorption technology was studied by batch adsorption process. Based on the results, the following conclusions can be drawn.

The handling of materials is very easy and harmless. The adsorption of chromium on the adsorbent used is effective at high concentration of adsorbate. The percentage of chromium removal increases with increases in contact time and lower pH in the range of 0.3 – 1.3. The efficiency of adsorption is increases with increase of concentration of surfactant sodium dodecyl sulfate some methods are used in removal of chromium from tannery waste water using adsorbent (lemon grass powder): The concentration of adsorbent increases the percentage of Chromium removal increases. Effect of concentration of adsorbate (tannery waste water): The concentration of adsorbate (chromium in tannery waste water) increases the adsorption decreases. Effect of contact time: the percentage removal increase with increases in contact time and this confirms that the rate of adsorption process is very high at longer period. Effect of pH low pH: The percentage removal very low. At particular pH, the percentage removal is maximum and this shows that adsorption is effective at pH less than 0.5. Effect of surfactant: The above graph shows that the percentage removal decreases with the increase of concentration of surfactant sodium dodecyl sulfate (SDS).

From the kinetic data pseudo second order well fitted than pseudo first order which showed that the chemisorption is rate controlling .the results obtained fitted well in both Langmuir and Freundlich adsorption isotherms. The correlation coefficient (R²) of this plot was found to be 0.988 and 1. This shows that it is highly correlated.From the above results it is concluded that the experimental conditions are very simple and operational cost is low. The proposed technology is economically feasible and eco-friendly in nature. The percent removal of chromium in aqueous solution is 95% with the effective dose of 2g lemon grass powder of adsorbent.
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