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ADSORPTION STUDIES OF SOME DYES AND METAL COMPLEXES ON GARLIC HUSK- A CHEAP NATURAL ADSORBENT

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ABSTRACT

The present work deals with the adsorption study of some metals and dyes on cheap natural adsorbent- the garlic husk, which is treated with acid before adsorption process. Metals are made to react with ligand which gives colored solution and was used for adsorption studies. The reagents were kept in contact with adsorbent reacted in presence of acidic or alkaline or in neutral condition. pH condition will be different for different metals and dyes, depending on the rate of adsorption. Along with this, other parameters like effect of dose, concentration of adsorbate, contact time etc are studied and found that the adsorption increases with dose and contact time but decreases with concentration. The adsorption isotherm studies like Frendlich and Langmuir model were found to be favorable.

INTRODUCTION

Trace metals are persistent contaminants, once added to the environment, they are not readily converted into harmless products. Removal of toxic heavy metals from industrial waste water has been practiced for several decades. The conventional removal methods such as chemical precipitation, electroplating, membrane separation, evaporation or ion exchange resins, are usually expensive and sometimes not effective. The presence of dyes has been a problem in the industries. Some of the dyes are not only aesthetic pollutants, but coloration by the dyes may interfere with light penetration affecting aquatic ecosystem. Hence, color removal of dyes from aqueous solution becomes one of the major environmental concerns. There are various methods for removing of dyes using conventional methods including coagulation and flocculation, oxidation or ozanation and membrane separation (Yasin *et al.,* 2010). In contrast, an adsorption is by far the most versatile and widely used and has proven successful in removing dyes and metal complexes from aqueous solutions. Numerous studies have been carried out by different researchers like, Areca nut shell (Geetha *et al.,* 2009), Egg shell (Geetha and Belagali, 2010) Prosopis cineraria (Gupta *et al.,* 2010), Tamarind kernel powder (Gupta and Sharma, 2010), Morus plant (Gopalswami *et al.,* 2010), Terminalia catappa (Kalpana *et al.,* 2010), Salvadora persica (Daga *et al.,* 2010), Moringa oleifera (Bhanupriya *et al.,* 2012). Literature survey reveals that there is no single adsorbent to remove many metals or dyes with maximum adsorption capacity (about 99%) and the garlic husk removes nearly nine dyes and twelve metal complexes. The garlic is grown in almost all the areas and is not at all used by any other researches and hence, the present study is carried out, for the removal of some dyes and metal complexes.

MATERIALS AND METHODS

Processing of garlic husk

Freely available garlic husk was cleaned and then treated with 2N HCl (acid activation). Washed thoroughly with distilled water, squeezed and then air dried, slightly powdered and then used for adsorption process.

Preparation of dye solutions

All the dyes were prepared for 100 ppm by weighing 0.1g each of the substances and dissolving separately in one liter, which further was diluted to required concentrations.

Preparation of metal solutions

Ammonium molybate (0.1288g) was weighted and dissolved in 100 mL of distilled water to which potassiumdihydro phosphate (0.0439g), stannous chloride (0.01mg) are added to give 100 ppm of ammonium phosphomolybdate solution. To this solution, 5 mL concentrated sulfuric acid solution was added to give blue color. The above solution was diluted and used for adsorption studies.

Potassiumdichromate (0.0124g) was dissolved in 100 mL of distilled water to which diphenyl carbazide (0.2%) (20 mL) was added with 1:1 sulfuric acid (5mL). The dark pink color develops. The solution was used for adsorption study of Chromium by diluting to the required concentrations.

Aluminium sulphate (0.233g) was dissolved in 100 mL of distilled water, to which Alizarin red dye solution (20 mL of 100ppm) was added along with 5 mL of concentrated hydrochloric acid (5 mL). The solution gets orange color, which was used for adsorption studies.

Calcium carbonate (0.0249g) and magnesium sulphate (0.1014g) were weighed and hydrochloric acid (2-3 drops) was added to dissolve the calcium carbonate and the solution was diluted to 100 mL, which gives 100 ppm of calcium and magnesium solutions. To the above solution, two or three total hardness tablets are powdered and added, to give wine red color on adding E.D.T.A (0.372g). The solution becomes blue and was used for the adsorption study of calcium and magnesium by diluting to required concentrations.

Zirconium oxychloride (0.3g) was added to 50 mL distilled water. Dissolve separately alizarin red (0.07g) in 50 mL distilled water, add this to zirconium solution and dilute to 1000 mL, which gives 100 ppm solution. Further diluted to required concentration for adsorption process.

Cupric sulphate (0.0392g) was dissolved in 100 mL of distilled water to which, Zincon reagent (0.02 % of 30 mL) was added to give blue color. It was further diluted and used for adsorption process.

Cobaltous sulphate was dissolved (0.02630g) in 100 mL of distilled water, which gives 100 ppm of cobalt solution. For this solution, 35% of ammonium thiocyanate in 100 mL of acetone: water (1:1) was added to give greenish blue color. It was further diluted and used for adsorption process.

Mercuric chloride (0.0135 g) was dissolved in 100 mL distilled water, to which 20 mL of 1,5-diphenylcarbazide solution was added to give violet color. 4N Nitric acid (3-4 mL) was added, the solution becomes colorless, which was used for the adsorption studies.

Cadmium sulphate (0.03713g) was dissolved in 100 mL distilled water to which 1, 5-diphenyl carbazide (10 mL) (0.25 % in acetone) was added, pH 10 was maintained by adding ammonia buffer solution, to give orange red color and was used for adsorption studies.

Nickel chloride (0.04049g) was dissolved in 100 mL distilled water, to which 0.01g of Zincon reagent (0.02%) was added, to give violet color. This solution was used for adsorption studies.

Zinc chloride (0.02150g) was dissolved in 100 mL of distilled water, to which 0.02% Zincon reagent (50 mL) was added, to give blue color. It was directly used for adsorption studies.

Ferrous ammonium sulphate (0.07022g) was dissolved in 100 mL distilled water, which gives 100ppm of iron solution. For this, 20 % of ammonium thiocyanate solution (30 mL) was added. The blood red color of iron solution was used for adsorption studies.

Adsorption isotherms

In order to determine the sorption potential of adsorbent, the study of sorption isotherm was essential in selecting an adsorbent for the removal of the metals or dyes. The adsorption data was studied with the Freundlich and Langmuir's isotherms (Adamson, 1960).

Freundlich isotherm: $\log q_e = \log K + (1/n \log C_e)$

Langmuir isotherm: $C_e/q_e = (1/Q_o b) + (C_e/Q_0)$

where, q_e - amount of metals or dyes adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K and n are respectively, the measures of sorption capacity and intensity of adsorption, C_e equilibrium concentration of metals or dyes (in mg/L), Q_o and 'b' are the Langmuir's constants indicating the sorption capacity (in mg/g) and energy of adsorption (in g/L) respectively from the slope and intercept.

Kinetics of adsorption

The adsorption kinetics was found to be of first order. The following equation proposed by Kannan and Vanangamudi (1991) was employed for adsorption data:

$K_1 = (2.303/t) \log (C_o/C_t)$

where, C_o and C_t are concentrations of metals or dyes at zero and time t (min). The values of $\log (C_o/C_t)$ were found to be linearly correlated with the contact time for different dyes and metals.

Further, the essential characteristics of the Langmuir isotherms can be described in terms of a dimensionless constant, namely separation factor or equilibrium parameter, R_L which was defined by Weber and Chakravarti (1974) in the equation, $R_L = 1/(1+bc_i)$, where, b is the Langmuir's constant and C_i is the initial concentration of metals (in ppm). The value of the parameter, R_L indicates the nature of the isotherm as given below:

Batch experiment

R_L value	Nature of Isotherm
$R_L > 1$	Unfavorable
$0 < R_L < 1$	Linear
$R_L = 1$	Favorable
$R_L = 0$	Irreversible

The values of the above equations are given in Table 4

Metals or dyes adsorption experiments were conducted in batch mode with 50 mL stock solution. The variables studied were adsorbent dose, concentration of adsorbate, pH and contact time. The mixtures were observed for adsorption process, after keeping the solutions for adsorption to take place.

RESULTS AND DISCUSSION

The effect of parameters like pH, dose of adsorbent (Fig.1), concentration (Fig. 2) and contact time (Fig. 4) on the removal of metals and dyes in aqueous media are investigated.

pH is an important parameter for dyes and metals adsorption phenomena in aqueous solutions. The effect of pH on dyes and metals adsorption was studied with pH 2, 7 and 9. Concentration and dose were kept constant.

Different dyes and metals react with H^+ and OH^- ions and the following observation were found.

Methylene blue do not change in color for any of the pH conditions, but the rate of adsorption is very fast in acidic medium.

Table 1: pH maintained for metal complexes to give color

pH	Acidic condition (2-6)	Basic condition (8-10)	Without adjusting pH.
Metals	Molybdenum, Chromium Aluminium, Cobalt, Mercury, Iron	Calcium, Magnesium Cadmium	Copper, Nickel, Zirconium, Zinc

Table 2: Contact time maintained for adsorption

Metals and Dyes	Adsorption period in h
Zinc, Lead, Aluminium, Molybdenum, Methylene blue, Bromothymole blue, cotton blue and Pararosaniline	24h
Iron, Chromium, Calcium and Magnesium, Copper, Cobalt, Mercury, Cadmium, Nickel, Zirconium, Alizarin Red, Indigo carmine and Bromocresol green	48h
Giemsa's stain	72h

Alizarin red in acidic medium turns yellow, dark pink in basic and red in neutral condition.
Pararosaniline in basic medium turns colorless, in acidic it turns dark pink and in neutral it will be in red color.
Cotton blue in acidic and neutral conditions does not change but, in basic it becomes colorless.
Bromocresol green in acidic medium turns to yellow, basic medium to blue and in neutral to algal green.

Bromothymol blue will also become yellow in acidic, in basic medium blue and in neutral, orange color.

Giemsa's stain do not change color for any pH condition but, low adsorption in acidic, than in basic and neutral conditions.

Indigo carmine, in basic medium gives greenish blue color while in acidic and neutral color do not change.

For metal solutions, pH was an important factor to form complex with reagents. The metal reacts with reagents either in acidic, basic or in neutral media to form a colored complex. pH maintained for different metal solution is shown in Table 1. Hence, different pH conditions were maintained for different dyes, during adsorption process.

Five numbers of 50mL samples of 100 ppm/L metal or dye solutions were taken in beakers and 1-5g of doses of adsorbent were added and studied for adsorption. In case of all dyes and metal adsorptions, as dose increases, adsorption increases (Fig.1).

Constant dose of adsorbents (2.0g) was separately added to 50mL samples with different concentrations of dye/metal solutions (20, 40, 60, 80 and 100ppm) in 5 beakers at room temperature and studied the adsorption process, which

Table 3: Statistical analysis of Co-relation co-efficient values for all metals (R values)

Parameters	Co-relation Coefficient (R) value for both Metals and Dyes.
Effect of adsorbent dose	1.00 and 0.999
Effect of concentration	-0.9491 and -0.9529
Effect of contact time	1.00 and 1.00
Co-relation of dose of adsorbent and concentration of metal solution	0.904 and 0.972

Adsorption pattern found in all the metals were similar

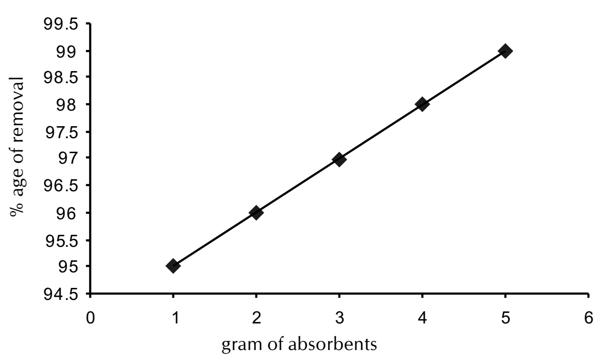

Figure 1: Effect of adsorbent dose for all dyes and metals

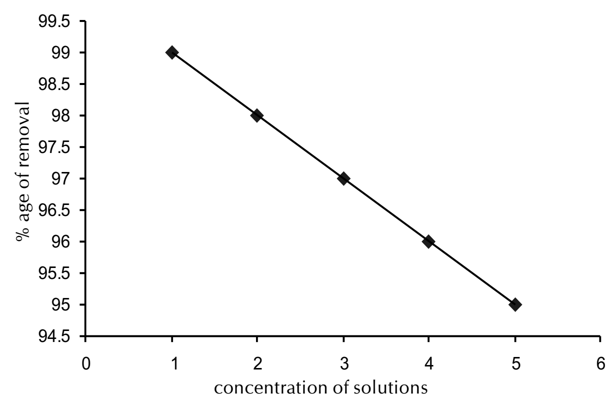

Figure 2: Effect of concentration of adsorbent for all dyes and metals

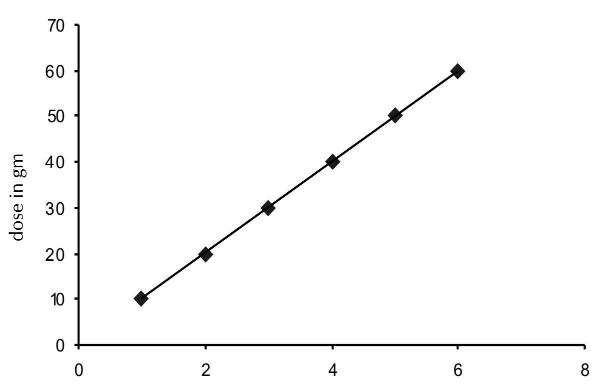

Figure 3: Effect of dose Vs concentration for all dyes and metals

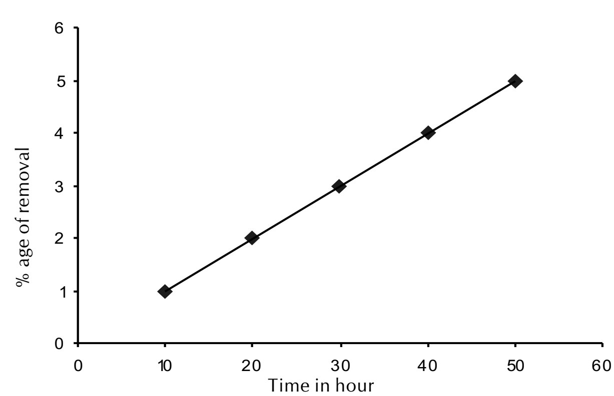

Figure 4: Effect of contact time for all dyes and metals

indicates that, as concentration increases the adsorption decreases for all the metal and dye solutions (Fig. 2).

Five number of 50 mL samples of dye or metal solutions from 20-100 ppm and varying doses of adsorbents from 1-4g were added in series. Then, the solutions were kept for adsorption process. The results are shown in figure 3 which indicates that, the dose and the concentration of all metals and dye solutions are co-related to each other.

The effect of contact time with 1.0g adsorbent dose in 50 mL of 10 ppm dye solutions was investigated. The adsorption increased with increase in time. Contact times of dye solutions are shown in Table 2 and Fig. 4.

The adsorption mainly depends on the dose and contact time. The Langmuir and Frendlich adsorption models were well fitted and R_L value shows that, the model developed is favorable. When compared to other adsorbents, the maximum removal of dyes and metals were found in the garlic husk, which is cost free adsorbent.

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