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Investigation on the capability of Silkworm Pupa as a Natural Adsorbent for Removal of Dyes from Textile Effluent

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Abstract

Recently, use of naturally-occurring low-cost and harmless material for removal of trace contaminants from colored wastewater has attracted extensive attention. In this study, silkworm pupa has been used as a basic dye adsorbent. Adsorption capacity and isotherms have been assessed. Results show that adsorption isotherms can be expressed well by Langmuir equation. The effects of parameters such as pH, temperature, agitation time and speed on the adsorption efficiency were investigated. It was found that among those factors the pH is the most pronounced one. Also the adsorption capacity of pupa towards the various cationic dyes is changed as follows: basic blue >basic yellow >basic red.

Keywords: *Adsorption, Isotherm, Color Removal, Silkworm Pupa, Basic Dyes, Wastewater*

Introduction

Textile effluents are among the most polluting industrial wastes and disposal of such wastes requires much attention[1]. The effluents from the dyeing and finishing processes are known to contain color, high amounts of surfactants, dissolved solids and possibly heavy metals such as Cr, Ni and Cu [2,3]. So the textile industry is continuing concern for the environment [3]. From an environmental point of view, the removal of synthetic dyes is of great concern, because some dyes and their degradation products are considered to be carcinogens [2,4] and toxic. Consequently, in their treatment not only bio-degradation should be taken into account, but also complementary methods of treatment are required. On the other hand, dyes impede light penetration, which can affect the photosynthetic activity of aquatic plants and raise the chemical oxygen demand [2,4,5]. So the dyes must be eliminated not only because of their toxicity but also mainly due to their visibility [6].

Several difficulties are encountered in removal of dyes from wastewater. By design, dyes are highly stable molecules, made to resist degradation by light, chemical, biological and other exposures [3]. Recently, the possibility of an adsorption process to

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remove dyestuffs discharged from textile industries has been considered [7] and it has been found that adsorption is superior to other techniques [2,8]. At present there is growing interest in using low-cost, commercially-available materials for the adsorption of dyes [9]. Although the most widely used industrial adsorbent is activated carbon but it is expensive and its filtration and regeneration is not cost- effective. A wide variety of materials such as fly ash, peat, phenolic resins, maize cob, activated sludge, natural clays, wood chips, sugar beet pulp, olive mill product, cellulosic materials, chitin, chitosan, rice husk, coconut shell, alginate, saw dust, lignite, cotton waste, teak wood bark, boiler bottom ash, sulphonated coal, sphagnum peat, zeolite, orange peel, egg shell and bentonite have been used as adsorbents for removal of dyes, heavy metals and other contaminants [1,2,4,5,9,13]. In this work, the possibility of using silkworm pupa, which is the waste of silk spinning industry, as an adsorbent for dyes removal from their aqueous solution has been investigated. Because of amino acid nature of pupa, it was predicted that it could have a reasonable capability for dye adsorption. Because of the nature of cationic dyes, the adsorption efficiency of different adsorbents towards them has been reported to be low[14]. Due to this shortcoming, it was decided to study elimination of basic dyes by silkworm pupa. The common analysis of silkworm pupa is shown in Tables 1 and 2. Figure 1 shows silkworm pupa in original and powder forms. Adsorption study was carried out by assessment of two adsorption isotherms, i.e., Langmuir and Freundlich.

Materials and Methods

1. Adsorbent and Dyes

Iranian silkworm pupa wastes, obtained from silk spinning process, were washed, dried, and ground. The powdered pupa was sieved and used as an adsorbent. Basic dyes included C. I. Basic Red 46, C. I. Basic Yellow 28 and C. I. Basic Blue 41(commercial grades).

2. Adsorption Studies

Batch sorption studies were carried out by agitating 400 ml of dye solutions of different concentrations and 1g of dry pupa powder in a 1-lit beaker for 2.5 hr at room temperature (25 °C). After reaching equilibrium, dye solutions concentrations were measured by a spectrophotometer in the maximum wavelength. Two adsorption isotherms (Langmuir and Freundlich) were fitted and adsorption equation constants were determined. Parameters such as agitation time and speed, pH and dye concentration were studied.

Results and Discussion

The general adsorption isotherm is shown in Figure 1. The time to reach equilibrium was found to be about 2.5 hours. To determine which isotherm can be fitted to these data, the linear form of Freundlich and Langmuir equations[16,17] (equation 1 and 2, respectively) were applied and regression coefficients of two curves were calculated:

$$\frac{m}{x} = \frac{1 + bC_e}{aC_e} = \frac{b}{a} + \frac{1}{aC_e} \quad (1)$$

$$\frac{x}{m} = kC_e^{\,n} \quad (2)$$

where $\frac{x}{m}$ is the amount of adsorbed material per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of solution (mg/l), a and b are Langmuir constants, and k and n are Freundlich constants.

The results are shown in Figures 2 and 3 and Tables 3 and 4. As is shown, although both Langmuir and Freundlich isotherms can be fitted to experimental data, the former is the

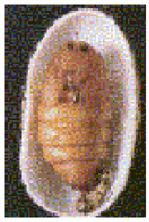
Table 1. Silkworm pupa protein nutrition components[15].

Project	Unit	Result	Project	Unit	Result
Protein	%	83.75	Zinc	ppm	18
Fat	%	2.38	Phosphor	ppm	10
Water	%	3.11	Calcium	ppm	3.312
Ash	%	5.11	Magnesium	ppm	11.250
Other	%	5.65	Iron	ppm	175

Table 2. Silkworm pupa protein amino acid analysis.

Amino acid	Silkworm pupa protein%	Amino acid	Silkworm pupa protein %
Threonine	3.58	Aspartic acid	9.32
Sulphur amino acid	3.97	Serine	3.30
Valine	2.78	Glutamic Acid	8.69
Isoleucine	3.69	Proline	2.43
Leucine	6.14	Glycine	3.95
Tryptophan	9.50	Alanine	3.79
Lysine	5.84	Histidine	1.66
Arginine	4.70		


a


b

Picture 1. Silkworm pupa: a) original form b)powder form.

most suitable one for all the three dyes, according to the values of R^2. Parameters related to each isotherm have been shown in Table 3. Maximum capacity of dye adsorption for pupa can be calculated from Langmuir isotherm parameters, *i.e.* Q=b/a. It is clear that the capacity of the adsorbent for the basic blue dye is the greatest.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium paramete R_L, which is defined by equation 3[18]:

$$R_L = 1 / (1 + bC_o) \quad (3)$$

where b is the Langmuir constant and C_o is the initial dye concentration (mg/l).

The suitable R_L values were found to be between 0 and 1. the calculated value of R_L for each dye is listed in Table 5. In the present study, the computed values of R_L are observed to be in the range of 0-1, indicating that the adsorption process is favorable for this adsorbent. In the case of Freundlich equation, n values were found to be less than unity, indicating that the isotherms can be characterized by a convex Freundlich isotherm.

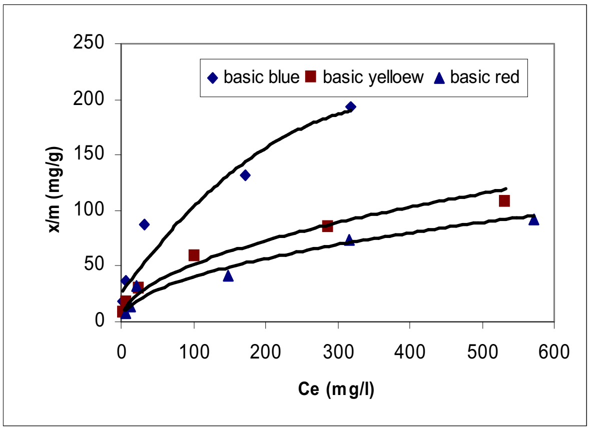


Figure 1. Basic dye adsorption isotherm of pupa.

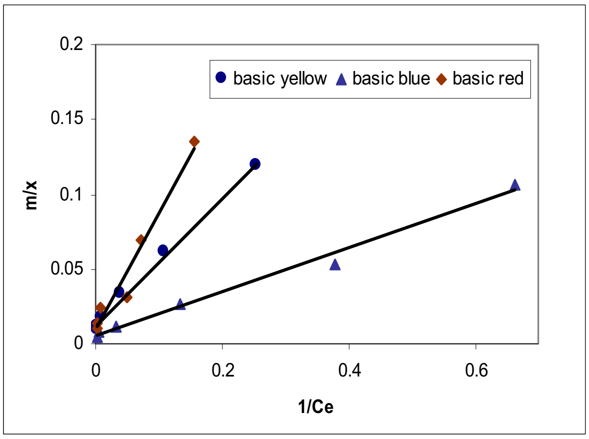


Figure 2. The linear form of Langmuir adsorption isotherm

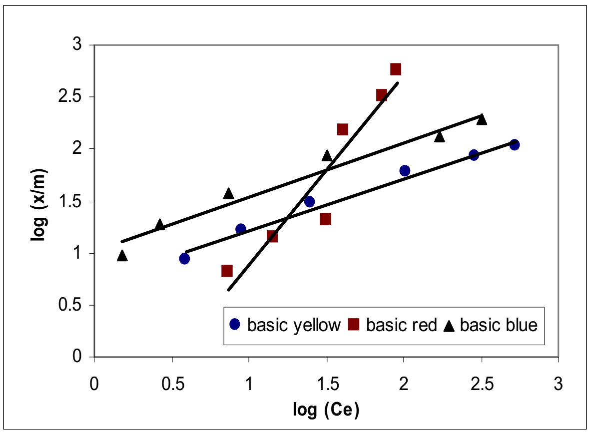


Figure 3. The linear form of Freundlich adsorption isotherm

Table 3. Langmuir adsorption isotherm parameters of dyes for the adsorbent.

Dyes (C. I. Basic)	**a**	**b**	**Q = a/b (mg/g)**	$\mathbf{R^2}$
Red 46	1.278	0.0124	103.1	0.9667
Yellow 28	2.355	0.0289	81.5	0.9948
Blue 41	6.835	0.0368	185.7	0.9884

Table 4. Freundlich adsorption isotherm parameters of dyes for the adsorbent.

Dyes (C. I. Basic)	**n**	**k**	$\mathbf{R^2}$
Red 46	0.49	4.1	0.9033
Yellow 28	0.51	5.1	0.9829
Blue 41	0.52	10.5	0.9587

Table 5. Equilibrium parameters for basic dyes.

C_0 *(mg/l)*	$\mathbf{R_L}$ **for Dyes (C. I. Basic)**		
	Red 46	**Yellow 28**	**Blue 41**
25	0.7633	0.5805	0.5208
50	0.6172	0.4089	0.3521
100	0.4464	0.2570	0.2136
250	0.2439	0.1215	0.0980
500	0.1388	0.0647	0.0515
800	0.0915	0.0414	0.0328

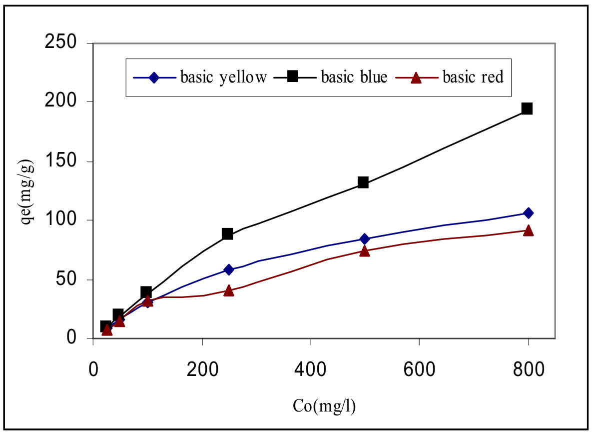


Figure 4a. Effect of initial dye concentration on adsorbed dyes

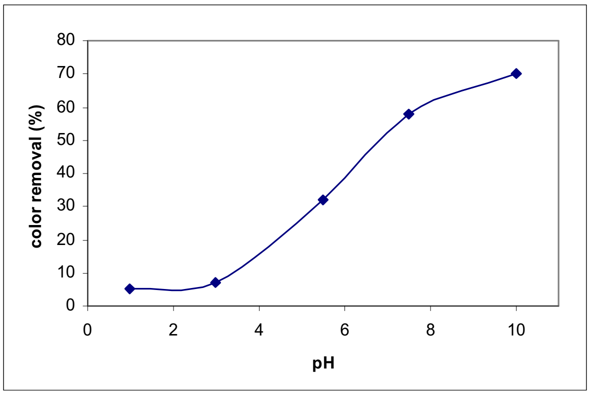


Figure 4b. Effect of pH on the basic dyes removal by silkworm pupa.

According to Figures 4 and 5 , by increasing the initial dye concentrations, the percentage removal decreases but the amount of adsorbed dye per unit mass of adsorbent (q_e) increases. This indicates that lack of available active sites (e.g., COO^-) for the high initial concentration, reduces removal. On the other hand, this phenomenon depends on the pH of the dye solutions that can affect ionization of acid and amino groups. The effect of initial pH of solutions is shown in Figure 4. As predicted , the figure shows that at low pH, adsorbent has a positive charge (acid groups are blocked with the positive charges). Therefore, there is repulsion between dye molecules (basic dyes) and adsorbent. So, the color removal will be low. By increasing pH, negative charge is created on the surface of adsorbent and because of the attraction between dyes and adsorbent, high color removal efficiency is achieved. Therefore, it can be suggested that the predominant mechanism of adsorption in this case is chemisorption.

Also, the effect of the agitation speed has been investigated. Figure 5 shows that although there is no significant change in color removal by increasing the agitation speed, there is an optimum speed at which adsorption will be at maximum. This difference is important for color removal and must be noticed. In fact, this difference varied between 5-12 % for different dyes. It is believed that at low speed, there is not enough effective contact between molecules of dyes and adsorbent. On the other hand, high-speed agitation can break bonds between dyes and adsorbent and cause reduction in color removal.

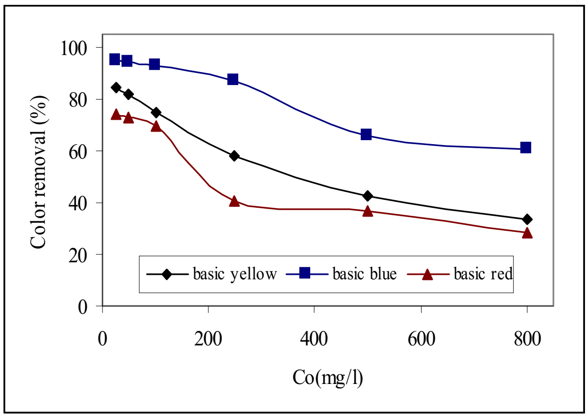


Figure 5a. Effect of initial dye concentration on color removal

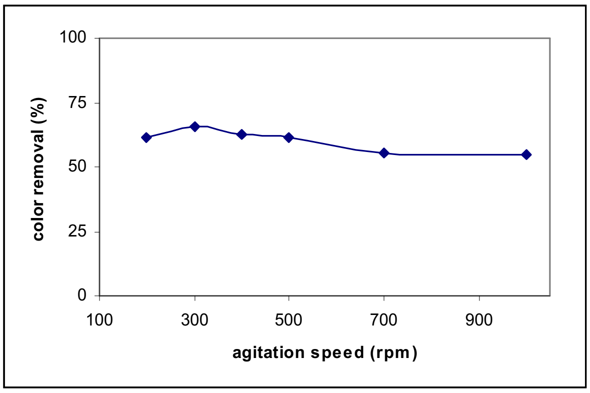


Figure 5b. Effect of agitation speed on color removal (C. I. Basic red 46).

Conclusion

In this study, it has been found that silkworm pupa has a fairly good adsorption property for basic dyes. Parameters such as pH, agitation time and speed of agitation have been investigated. The most important factor for this adsorbent is pH of the solution. This effect can be related to the amino acid nature of silkworm pupa. So, by pH adjustment it can be used for other dye classes, as well.

References

1. Annadurai, R. Juang, and D. Lee, advance in environmental research, No. 6, 2002, 191-198.
2. N. Kannan, M. M. Sundaram, Dyes and Pigments, 51, 2001, 25-40.
3. B. Smith, T. Koonce, S. Hud, Amer. Dyestuff. Rep., October, 1993, 20-34.
4. R. Sanghi, B. Bhattacharya, Coloration technology, 118, 2002, 256-238.
5. R. Sivaraj, C. Namasivayam, K. Kadirvelu, Waste management, 21, 2001, 105-110.
6. L. C. Morais, O. M. Freitas, E. P. Goncalves, L. T. Vasconcelos and C. G. Gonzales Beca, Wat. Res., 33(4), 1999, 979-988.
7. K. D. Bhavani, P. K. Dutta, Amer. Dyestuff. Rep., April. 1999, 53-58.
8. L. Markovska, M. Mincheva, V.
9. Meshko, Proceedings of the cond Pacific Basin Conferences on Adsorption Science and chnology, 2001, 406-411.
10. Z. Al-Qodah, Wat. Res., 34(17), 2000, 4295-4303.
11. G. Mckay, H. S. Blair and R. Gardner, J. Appl. Polym. Sci., 29, 1984, 1499-1514.
12. J. Scott, D. Guang, K. Naeramitmarnsuk, M. Thabuot and R. Amal, J. Chem. Technol. Biotechnol., 77, 2001, 63-69.
13. K.H. Chu, J. Hazardous Materials, B90, 2002, 77-95.
14. P. Waranusantigul, P. Pokethiyook, M. Kruatrachue and E. S. Upatham, Environ-mental pollution, 125, 3(2003), 385-392.
15. R. Sanghi and B. Bhattacharya, Color. Technol., 118(2002), 47-58.
16. Projects from Liuhe Group Corporation (internet reference), 2002.
17. S. A. Figueiredo, R. A. Boaventura and J. M. Loureiro, Separation and Purification Technology, 20 (2000), 129-141.
18. 17. C.Namasivayam and D. Kavitha, Dyes and Pigmen Pigments 54 (2002), 47-58.
19. Namasivayam, R. T. Yamuna and D. J. S. E. Arasi, Environmental Geology, 41 (2001), 269-273.