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UTILIZATION OF UNWANTED TERRESTRIAL WEEDS FOR REMOVAL OF DYES

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ABSTRACT

Human welfare is adversely affected by unwanted and undesirable plants, which convert the useable land into a wasteland. The present study was an attempt to utilize unwanted weeds as a resource with the objective to evaluate the removal efficiency of two low cost adsorbents named as Raw *Parthenium hysterophorus* (RPH) and Raw *Saccharum munja* (RSM) for adsorption of dyes like Congo red (CR), Methylene blue (MB) and Crystal violet (CV). The batch study was carried out to study the impacts of various parameters like pH, adsorbent dose, initial dye concentration, contact time and shaking speed. The maximum adsorption for CR was 86% by RPH, MB was 98% and CV was 97% by RSM at dose 1g/100ml, 150rpm, dye concentration 50ppm, time 120 minutes and temperature 25℃ but optimized pH was varied according to dyes and type of adsorbents, it was ranged from 4 to 10. Adsorption isotherms were applied on the experimental data and found to be Freundlich isotherm was well fitted for RSM and RPH during MB dyes adsorption (r^2= 0.892 & 0.858) as compared to CR and CV dyes. Low-cost adsorbents have potential to adsorb dyes from wastewater and show applicability in wastewater treatment process.

Keywords: Adsorption, Wastewater, Congo Red, Methylene Blue, Crystal Violet, Adsorbent.

INTRODUCTION

Water pollution by dyes is becoming a worldwide problem nowadays because a large quantity of dyeing effluent is discharged into water bodies. Various industries including textiles, food, plastic, cosmetics, rubber, paper and pulp use chemicals during the processing of raw material, i.e. Dyes, organic colored compounds that impart color to various substrates. There is various type of dyes used in textile industries like reactive dye, direct dye, basic dye, acid dye, azo dye, mordant dye, disperse dye, vat dye and sulphur dye.[1] These dyes contain aromatic structure which provides stability to them, so they are non-biodegradable in nature.[2] The colored water caused due to dyes impair aquatic ecosystem as sunlight could not penetrate through colored water and affects photosynthetic activity. Dyes are also known to be mutagenic, carcinogenic and toxic in nature,[3] so there must be proper method for dye removal in textile industries as these are the main source of dye effluent discharge in nearby water bodies.

Various remediation processes have been employed for dye removal namely, nano-filtration, oxidation process, ion exchange, ozonation, ultrafiltration and coagulation, but these are not cost-effective and difficult to operate. Due to some drawbacks of remediation processes, adsorption process found to be best process due to its low cost, low maintenance and low generation of by-products. The highly used conventional adsorbent is activated carbon due to more availability of porosity, surface area and high adsorption rate. Nowadays, various non-conventional adsorbents are used in adsorption process depending on their low cost and abundance in nature. Low-cost adsorbents require little processing and found abundantly in nature. The various low cost adsorbents have been investigated by researchers like agricultural waste,[4] banana peel,[5] *Ficus carica,*[6] apple peels,[7] apricot stone,[8] bagasse fly ash,[9] peat,[10] abundant weeds,[11] walnut shell,[12] soya waste,[13] hen feather,[14] oil palm midrib,[15] sugarcane baggase,[16] *Typha angustifolia,*[17] natural zeolites,[18] sewage sludge,[19] etc. The objective of the present work is to study the adsorption of congo red (CR), methylene blue (MB) and crystal violet (CV) on dead biomass of weeds

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Parthenium hysterophorus and *Saccharum munja.* These weeds cause adverse effects on environment and human health. Pollens of these also cause respiratory problems and allergies. These are explored for useful purposes, i.e., removal of dyes from wastewater.

EXPERIMENTAL

Adsorbent Preparation

In this study, plants *Parthenium hysterophorus* and *Saccharum munja* were used as adsorbent, collected from a nearby area of Rohtak city for removal of dye from aqueous solution. To remove dirt and other impurities, washing was done by tap water followed by distilled water. Initially dead biomass of these plants was dried under sunlight then followed by drying in oven at 60^0C for 24 hours. Plants were crushed to make powder and sieved. These were washed with 1% formaldehyde to remove color then dried and stored in airtight containers. Characterizations of adsorbents have been done according to Allen.[20]

Dye Solution

The analytical grade dyes Congo red (CR), Methylene blue (MB), Crystal violet (CV) purchased from Central Drug House (P) Ltd. were used. Stock solution (1000mg/l) of dyes was made by dissolving 1g of dyes into 1 liter distilled water and serial dilutions were made with distilled water to prepare working solutions of different concentrations.

Batch Adsorption Study

Adsorption experiments were done to assess the effects of various parameters such as pH, adsorbent dose, contact time, the concentration of dye and shaking rate. To examine the effect of pH, time was kept 1hr, whereas dose was 0.5g/100ml at 25̊C with 150rpm and pH varied from 3 to 10. In case of optimization of dose, known amount of adsorbent doses were agitated with 100ml dye solution of 100ppm for MB and CV, whereas 20ppm for CR was taken in 250ml conical flasks at a speed of 150rpm at 25̊ C for 1 hour. To assess the impact of contact time, the study was conduct at 0.5g/100ml dose, pH 7 (RSM) and pH 4 (RPH) for CR, pH 10 (RSM) and pH 5 (RPH) for MB, pH 10 (RSM) and 8 (RPH) for CV at 150rpm and 25̊C. The effect of initial concentration and rpm was assessed by varying the concentration from 20 to 250mg/l and rotation from 50 to 250 at optimized conditions. After desired contact time, conical flasks were removed and allowed to settle down the adsorbent. The samples were filtered out using Whatman filter paper and filtrate was measured by using UV-visible spectrophotometer at 497 nm for CR, 590nm for CV and 665nm for MB. In this study, parameters included were pH(3-10), dose (0.2-1.2g), initial dye concentration (50-250mg/l), contact time (15-120min) and rpm (50-250) by varying one at a time and keeping others constant. The removal percentage of dye was calculated as removal efficiency:

$$\text{Removal (\%)} = ((C_0 - C_e) / C_0) \times 100 \qquad (1)$$

Where, C_0 and C_e are initial and final concentration (mg/l) of dye before and after adsorption, respectively. The amount of dye adsorbed on the surface of adsorbate was calculated as follows:

$$q_e \text{ (mg/g)} = (C_0 - C_e)V / x \qquad (2)$$

Where, C_0 and C_e are initial and final concentrations of the dye adsorbed (mg/l), V is the volume of the dye solution (Litre), q_e is the amount of dye adsorbed at equilibrium and x is the weight of the adsorbent(g).

Adsorption Isotherm

It is a batch equilibrium test that provides data relating to adsorbent adsorbed per unit weight to the amount of adsorbent in the solution. To describe the adsorption isotherm, Freundlich model was applied.
Freundlich isotherm: It assumes the adsorption of dye on the heterogeneous surface and there is no restriction to the formation of monolayer.[21] The linear form of the Freundlich isotherm is described by:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

Where, C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg/g) is the amount of dye adsorbed at equilibrium by the adsorbent, K_F (mg/g) and n are constants representing the adsorption capacity and intensity of adsorption.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The characterization of adsorbents is shown in Table-1. Raw *Parthenium hysterophorus* (RPH) was found slightly acidic very near to neutral point whereas, raw *Sachharum munja* (RSM) was more acidic in nature. The bulk density of RPH and RSM was found to be 0.353g/cm³ and 0.169g/cm³, respectively, which indicate that adsorbents were lighter in weight and contain more particle per gram while the particle density was noted as 0.383g/cm and 0.224g/cm³, respectively. The adsorbents solubility in water was recorded as 4.2% and 5.9% for RPH and RSM, respectively. Similarly, the solubility in acid was recorded as 7.5% and 8.4% for RPH and RSM, respectively.

Table-1: Characterization of Adsorbents Prepared from Weeds.

Parameters	*P.hysterophorus*	*S.munja*
pH	6.15	5.70
Bulk density g/cm³	0.353	0.169
Particle density g/cm³	0.383	0.224
Solubility in water (%)	4.2	5.9
Solubility in acid (%)	7.5	8.4
Porosity(%)	7.83	22.55

Effect of pH

The pH is the main parameter in the adsorption of dye. The removal percentage of various dyes at different pH is depicted in Fig.-1. The effect of pH was studied by varying pH from 3 to 10. The experiment was carried out by taking 0.5g of adsorbent agitating with 20ppm of Congo red (CR) and 100ppm of both Methylene blue (MB) and Crystal violet (CV) dyes at a speed of 150rpm for 1hour at 25̊C. For CR, Raw *Saccharum munja* (RSM) showed maximum removal 61.7% of dye at pH 7 and Raw *Parthenium hysterophorus* (RPH) showed 86.9% removal at pH 4.

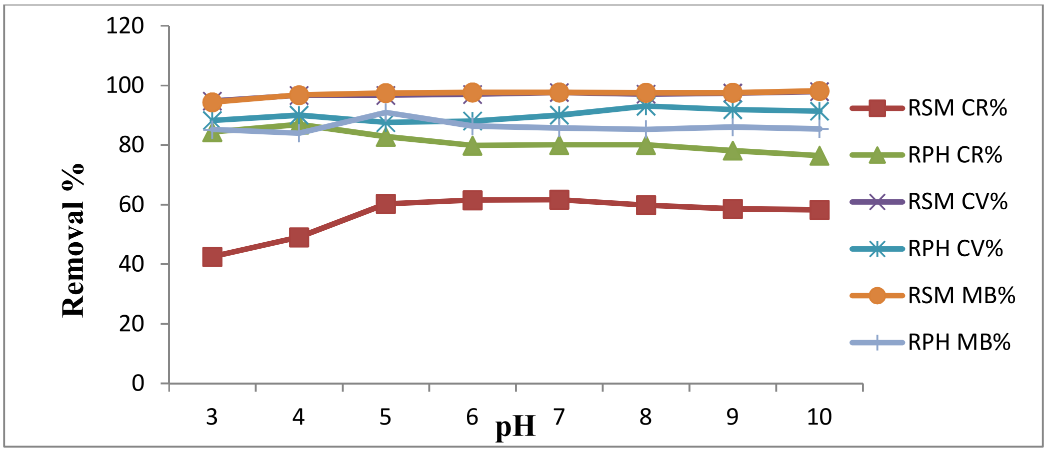

Fig.-1: Effect of pH on Removal % of Dye: Initial Dye Concentration CR(20mg/l), MB and CV (100mg/l), Dose (0.5g), Contact Time (60min), rpm (150) and Temperature (25^0C).

The maximum adsorption by CR at pH 7 could be due to a higher pH, the negatively charged sites were not favorable for dye adsorption due to electrostatic repulsion.[22] At lower pH than 4, dye adsorption would not favor because CR changes red to blue. Congo red showed maximum efficiency removal in neutral pH and minimum in basic pH due to presence of OH^- ions compete for adsorption sites with dye anions. For MB, RSM showed maximum removal 98.2% of dye at pH 10 and RPH 91% showed at pH 5. MB is cationic dye, when it dissolves in water gives positively charged ions. Adsorption of cationic adsorbate like MB opposed by positively charged surface of adsorbent in acidic medium. But when we increase the pH of solution, the surface of adsorbent acquires the negative charge which enhances the adsorption process of MB due to increasing in electrostatic attraction among the negative charges adsorbent and positively charged dye.[23-24] For CV, RSM and RPH showed maximum dye removal 98 and 93.1% at pH 10 and pH 8, respectively. It is evident from the results that there was significant variation in optimum pH for various dyes.

Effect of Dose

The adsorbent dose is also an important factor as it shows the adsorption capacity of adsorbent at initial concentration of adsorbate solution. As amount of adsorbent increases, adsorption rate increases because number of active sites for adsorption increases with increase in amount of adsorbent dose. The effect of adsorbent dose was studied by varying dose 0.2g to 1.2g at optimized pH, concentration 20ppm of CR and 100ppm for both MB and CV at a speed of 150rpm for 1hour at 25°C. Fig.2 illustrated that as amount of adsorbent dose increases from 0.2g/100ml to 1.2g/100ml the removal percentage increased from 22.9% to 93.7% for RSM, 33% to 67.3% for RPH for Congo red, 77.8% to 89.4% for RSM, 67.2% to 80.6% for RPH for Crystal violet and 76% to 89% for RSM, 69.7% to 89.5% for RPH for MB. Both adsorbents showed equilibrium saturation for dye removal at 1g/100ml of adsorbent.

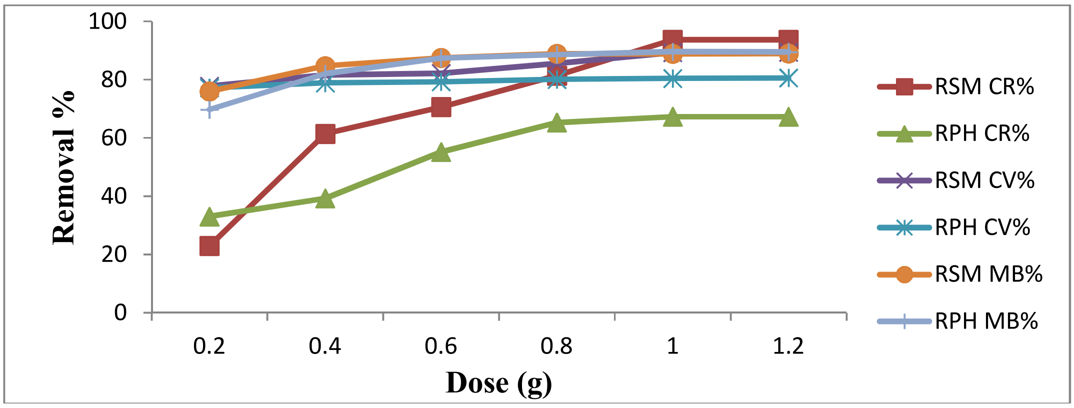

Fig.-2: Effect of Adsorbent Dose on removal % of Dye: Initial Dye Concentration CR(20ppm), MB and CV (100ppm), Contact Time (60min), rpm (150) and Temperature (25^0C) at Optimized pH.

Effect of Initial Dye Concentration

Figure-3 illustrated the effect of initial dye concentration on adsorption of dyes. The batch study was carried out by varying initial dye concentration from 50 to 250ppm by taking 1g of adsorbent agitating in a shaker for 1hour at 25°C with shaking speed of 150rpm. The result revealed that adsorption was maximum at 50ppm and after that adsorption percentage decreases. It is attributed to more availability of the adsorption sites[25] and adsorption sites become saturated with increased concentration of dyes. The maximum removal of CR by RSM and RPH were observed as 94.6 and 84.7%, respectively. For MB, maximum removal was found to be 93.9 for RSM and 90.4% for RPH, while in case of CV removal was 91.4% for RSM, 90.1% for RPH respectively.

Effect of Contact Time

Figure-3 shows the effect of contact time on adsorption of dyes by RSM and RPH. Contact time is the time which ensures the duration of agitation time which is sufficient for the adsorption process to reach equilibrium.[26] The rate of adsorption increases with increase in time and becomes constant after attaining equilibrium. This is attributed to the availability of adsorption sites followed by slower adsorption by attaining saturation level after equilibrium. RSM and RPH showed maximum removal percentage at 120 minutes by taking 20ppm of CR and 100ppm for MB and CV, 0.5g/100ml of adsorbent dose at 150rpm, 25°C temperature. Results revealed that maximum removal of CR by RSM and RPH was found to be 87.36 and 71.11%, respectively. Similarly, MB showed maximum removal of 92.1 and 85.56% by RSM and RPH, respectively. While, removal for CV was found to be 86 and 84.2% for RSM and RPH, respectively. The various dyes and adsorbents showed the Equilibrium/ saturated time at one hour.

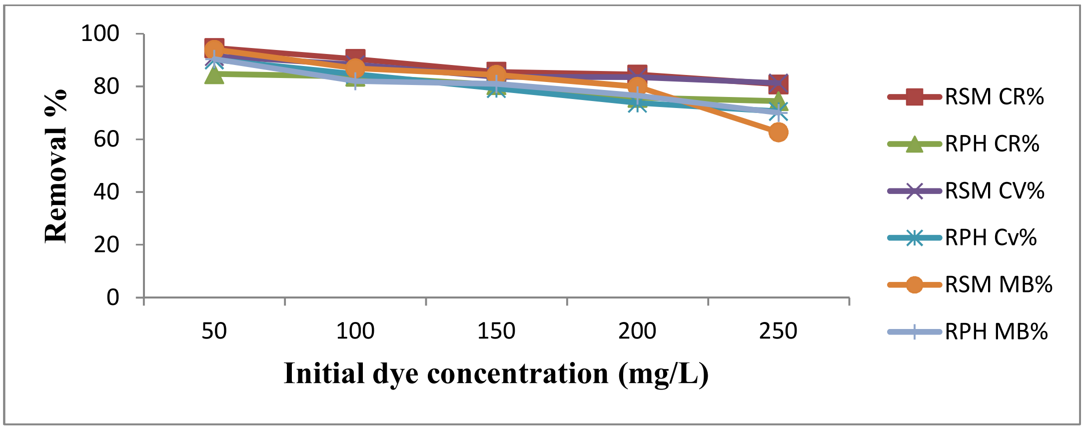

Fig.-3: Effect of Initial Dye Concentration on Dye Removal %: Dose (0.5g), Contact Time (60min), rpm (150) and Temperature (25^0C) at Optimized pH.

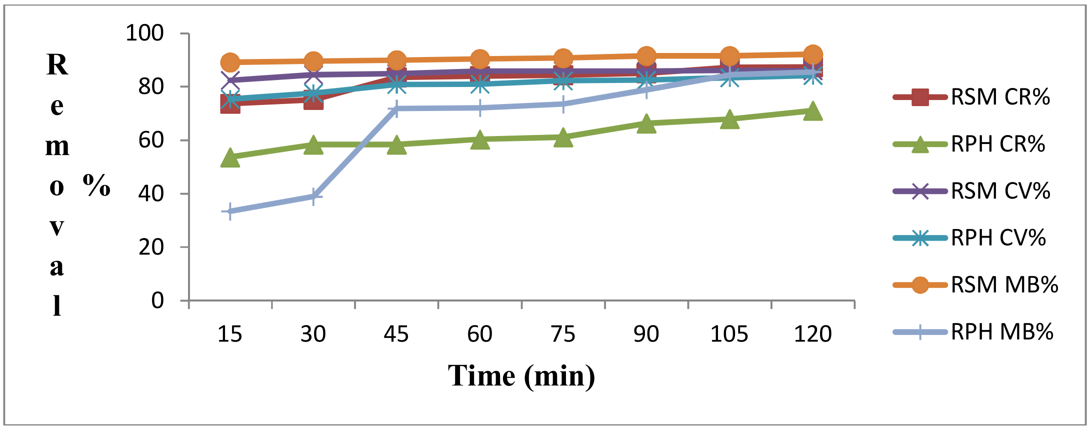

Fig.-4: Effect of Contact Time on Dye Removal %: Dose (0.5g), Concentration (20ppm for CR and 100 ppm for MB and CV), rpm (150) and Temperature (25C) at optimized pH.

Effect of RPM

The effect of rpm on dye removal as shown in Fig.-5. It showed that the maximum removal percentage for three dyes had been achieved at 250rpm, while equilibrium conditions were attained at 150 rpm. It is attributed that after a particular shaking rate, the removal of dye became saturated due to less availability of adsorption sites. RSM and RPH showed maximum removal of 95.8 and 80.6% for CR, respectively and similarly, 91.1 and 89.9% for RSM and RPH for MB. While in case of CV, the maximum removal was found to be 88.7 and 85.5% for RSM and RPH, respectively.

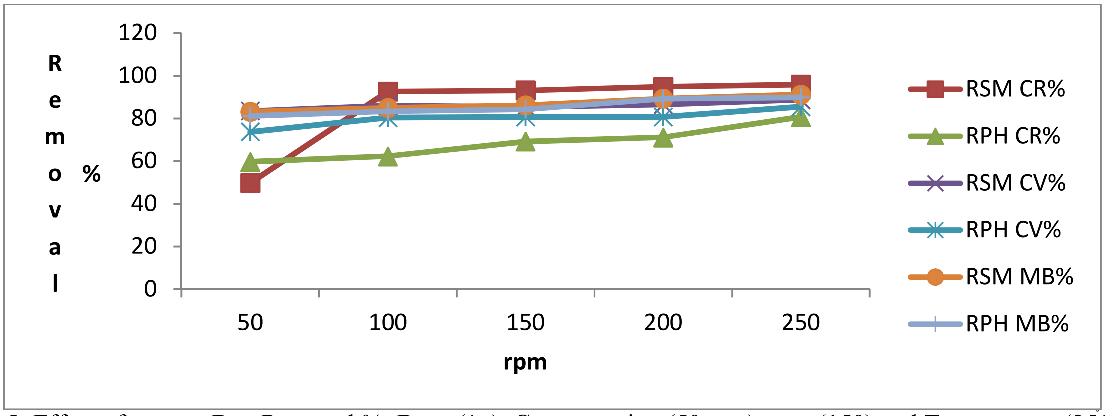

Fig.-5: Effect of rpm on Dye Removal %: Dose (1g), Concentration (50ppm), rpm (150) and Temperature (25C) at Optimized pH.

Adsorption Isotherm

Adsorption isotherm was conducted in this study to examine the adsorption mechanism. Freundlich isotherm was better fitted for MB as compared to CR and CV. The n value shows heterogeneity of the adsorbent surface and also depict favourable adsorption of dye. The K_f value suggests the dye-binding affinity of adsorbent. R^2 value indicates the equilibrium relationship between the amount of adsorbed dye and their equilibrium concentration in the solution.

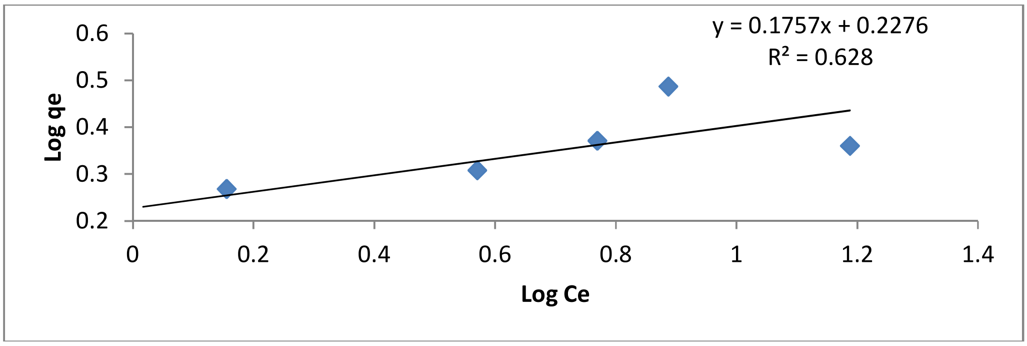

Fig.-6: Freundlich Plot for RSM on CR

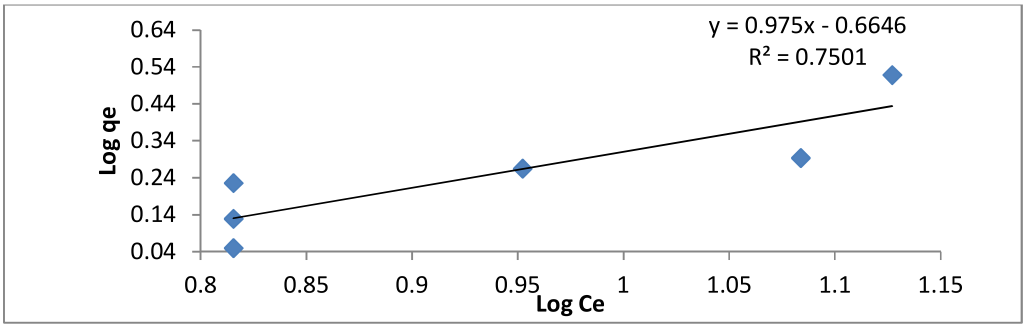

Fig.-7: Freundlich Plot of RPH on CR

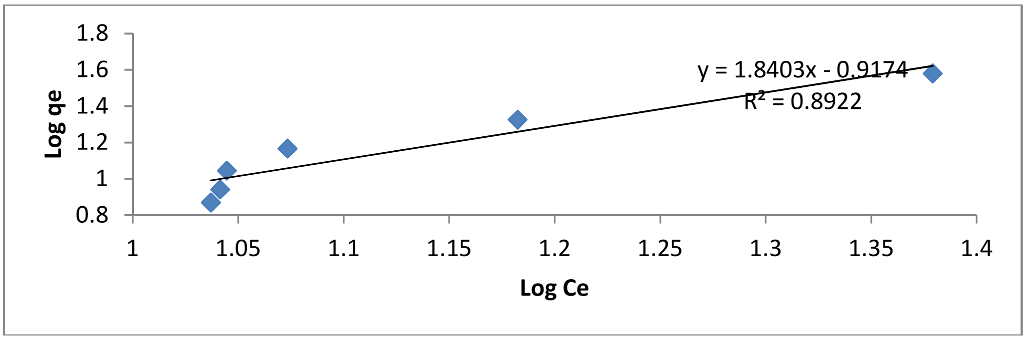

Fig.-8: Freundlich Plot of RSM on MB

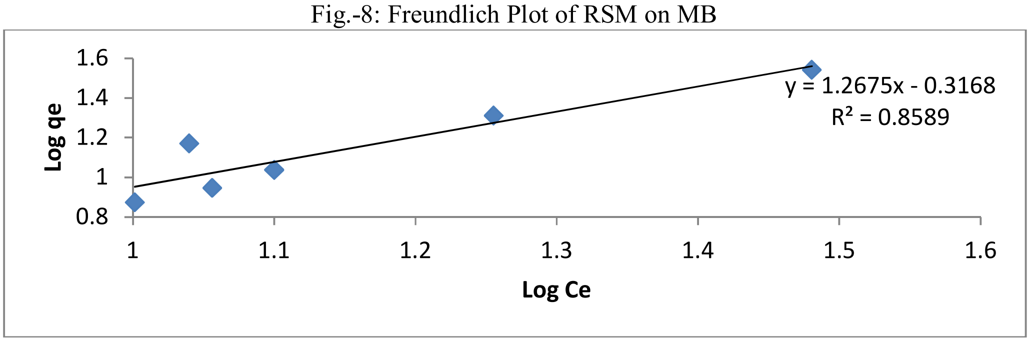

Fig.-9: Freundlich Plot of RPH on MB

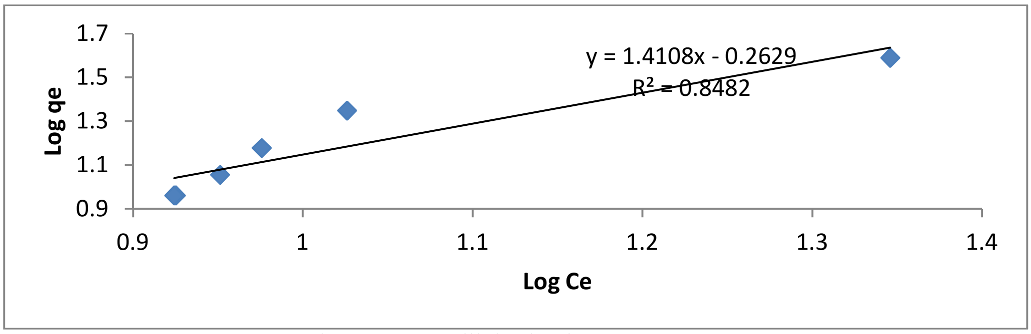

Fig.-10: Freundlich Plot for RSM on CV

Table-2: Rate Constant of Freundlich Isotherm for Different Dyes CR, MB and CV.

Dye	Adsorbent	K(mg/g)	N	R^2
Congo red (CR)	*Saccharum munja*	1.686	5.71	0.628
	Parthenium hysterophorus	4.61	1.02	0.750
Methylene blue (MB)	*Saccharum munja*	8.26	0.54	0.892
	Parthenium hysterophorus	2.07	0.78	0.858
Crystal violet (CV)	*Saccharum munja*	1.82	0.70	0.848

CONCLUSION

Colored effluent is a great threat to the freshwater bodies and needs to treat before discharge. It was found that powder prepared from Raw *Parthenium hysterophorus* (RPH) and Raw *Saccharum munja* (RSM) are good adsorbents for removal of dyes and can be used in wastewater treatment. On the other hand, *Parthenium hysterophorus* and *Saccharum munja* are unwanted weeds, which degrade the land quality and create various health problems in human beings. So, this study was an attempt to utilize these unwanted plants for dyes removal. The optimized parameters for maximum adsorption of Congo Red, Methylene Blue and Crystal Violet were found to be dose (1g), rpm (150), time (120minutes), temperature (25°C), dye concentration (50ppm) for both adsorbents. For Congo Red, RSM showed maximum removal of dye at pH 7 and RPH showed at pH 4, while optimum pH was 10 (RSM) and pH 5 (RPH) for Methylene Blue. Similarly, pH 10 (RSM) and pH 8 (RPH) were optimum for Crystal Violet, respectively. Freundlich isotherm was better fitted for Methylene Blue during adsorption by Raw *Saccharum munja* and Raw *Parthenium hysterophorus*.

REFERENCES

1. A. Demirbas, *J. Hazrd. Mater.,* **167(1-3)**, 1(2009), **DOI:**10.1016/j.jhazmat.2008.12.114
2. H. Chen, and J. Zhao, *Adsorption*, **15(4)**, 381(2009), **DOI:**10.1007/s10450-009-9155-z
3. A.M. Aljeboree, A.N. Alshirifi and A.F. Alkaim, *Arabian J. Chem*. In Press, (2014), **DOI:**10.1016/j.arabjc.2014.01.020
4. G. Annadurai, R. S. Juang and D. J. Lee, *J. Hazard. Mater*., **92**, 263 (2002), **DOI:**10.1016/S0304-3894(02)00017-1
5. N. K. Mondal, and S. Kar, *App. W. Sci.*, **8(6)**, 157 (2018), **DOI:**10.1007/s13201-018-0811-x
6. D. Pathania, S. Sharma and P. Singh, *Arabian J. Chem.,* **10(1)**, 1445(2017), **DOI:**10.1016/j.arabjc.2013.04.021
7. I. Enniya and A. Jourani, *J. Mater. Environ. Sci.*, **8(12)**, 4573(2017).
8. M. Abbas, and M. Trari, *Process Safety and Environmental Protection*, **98**, 424(2015), **DOI:**10.1016/j.psep.2015.09.015
9. I. D. Mall, V. C. Srivastava, N. K. Agarwal and I. M. Mishra, *Chemosphere,* **61**, 492(2005), **DOI:**10.1016/j.chemosphere.2005.03.065
10. H. I. Chieng, L. B. Lim and N. Priyantha, *Desalin Water Treat.,* **55**, 664(2015), **DOI:**10.1080/19443994.2014.919609
11. L. B. Lim, N. Priyantha, C. M. Chan, D. Matassan, H. I. Chieng, and M. R. R. Kooh, *Desalin Water Treat.*, **57(18)**, 8319 (2016), **DOI:**10.1080/19443994.2015.1017740

12. M. K. Dahri, M. R. R. Kooh and L. B. Lim, *J. Env. Chem. Engg.*, **2(3)**, 1434(2014), **DOI:**10.1016/j.jece.2014.07.008
13. M. R. R. Kooh, M. K. Dahri, L. B. Lim and L. H. Lim, *Arabian J. Sci. Engg.*, **41(7)**, 2453(2016), **DOI:**10.1007/s13369-015-1877-5
14. A. Mittal and J. Mittal, *Green Chemistry for Dyes Removal from Wastewater: Research Trends and Applications*, 409(2015), **DOI:**10.1002/9781118721001.ch11
15. M. L. Firdaus, E. Susanti, Ghufira, W. Alwi and E. Swistoro, *Rasayan J. Chem.,* **11(4)**, 1532(2018), **DOI:**10.31788/RJC.2018.1144030
16. M. Mathivanan and S. E. Saranaathan, *Rasayan J. Chem.,* **11(2)**, 877(2018), **DOI:**10.31788/RJC.2018.1122086
17. M. Santhi, P. E. Kumar and M. Sathya, *Rasayan J. Chem.,* **11(4)**, 1423(2018), **DOI:**10.31788/RJC.2018.1143066
18. Y. A. B. Neolaka, E. B. S. Kalla, G. A. Malelak, N. K. Rukman, G. Supriyanto, N. Y. T. Puspaningsih, *Rasayan J. Chem.,* **11(2)**, 494(2018), **DOI:**10.31788/RJC.2018.1121994
19. M. Otero, F. Rozada, L. F. Calvo, A. I. Garcıa and A. Moran, *Dyes and Pigments*, **57(1)**, 55(2003), **DOI:**10.1016/S0143-7208(03)00005-6
20. Allen, S. A., Chemical Analysis of Ecological Materials, Blackwell, London (1989).
21. H. Freundlich, *J. Phy. Chem.*, **57**, 385(1906).
22. M. Arami, N. Y. Limaee, N. M. Mahmoodi and N. S. Tabrizi, *J. Hazrd Mater.*, **135(1-3)**, 171(2006), **DOI:**10.1016/j.jhazmat.2005.11.044
23. M. M. Abd El-Latif and A. M. Ibrahim, *Desalin Water Treat.*, **6(1-3)**, 252(2009), **DOI:**10.5004/dwt.2009.501
24. P. K. Malik, *Dyes and Pigments*, **56(3)**, 239(2003), **DOI:**10.1016/S0143-7208(02)00159-6
25. M. Mulugeta, B. Lelisa, *Mod. Chem. Appl.*, **2(4)**, 146 (2014), **DOI:**10.4172/2329-6798.1000146
26. M. R. R. Kooh, M. K. Dahri and L. B. Lim, *Appl. Water Sci.*, **7(7)**, 3859(2017), **DOI:**10.1007/s13201-017-0537-1

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