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Research article

EXTRACTION OF METHYLENE BLUE DYE FROM POLLUTED WATERS USING SOME BIO-ADSORBENTS

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ABSTRACT : Sorbents derived from roots of Tephrosia purpurea, leaves and stems of Terminalia Arjuna and Bivalve snail shells have been explored for their sorption abilities towards Methylene Blue using synthetically prepared simulated waste waters. It is found that at high pHs, these bio-materials have shown strong affinity towards Methylene Blue. The physicochemical properties such as pH, sorbent concentration and time of equilibration have been optimized for the maximum removal of Methylene Blue from waste waters. Methodologies have been developed to extract good quantities of the dye. The roots powder of Tephrosia Purpurea has been proved to very effective even at 1.0 gm/500 ml of the sorption concentration at pH :8 or 10. More than 95.0% of extraction of Methylene Blue has been found with the bark powders of Terminalia Arjuna at all pH of study viz., 2-10. Interference of Fivefold excess of common anions and cations present in natural waters, have been studied. Anions have not interfered while Cation like Ca^{2+}, Mg^{2+} and Cu^{2+} have shown some interference but Fe^{2+} *and* Zn^{2+} have synergistically maintained the maximum extraction of the dye. The procedures developed have been successfully applied to some industrial effluent.

Key Words: Methylene Blue; pollution control; bio-adsorbents; applications.

INTRODUCTION

The removal of dyes from effluents of textile, paper, plastic and cosmetic industries is one of the active areas of pollution control research. Most of the synthetic dyes are not bio-degradable [Banat et al, 1996] and toxic. Their possible contamination of water bodies around the dye based industries is causing the environmental concern (Ho and McKay, 1998; Walker et al., 2003; Stydini et al., 2004).

Methylene Blue (MB) is extensively used in coloring of paper, cottons, and wools and in preparing hair colorants. If the effluents from the industries related to these, are not adequately treated, Methylene Blue is leaked into the nearby water bodies and due to its non-biodegradable nature, it gets accumulated and turns to be a treat to aquatic life. Methylene Blue is hazardous to human beings and causes the rise of heartbeat, vomiting, shock, cyanosis, jaundice, quadriplegia, tissue necrosis and even cancer (Albanis et al., 1988, Boeningo, 1994). The color of the dye prevents the visible light to reach to the aquatic life in waters and thereby blocks some photo-sensitive bio-chemical reactions essential for sustaining in aquatic life.

The controlling of the dye pollution using conventional methods based on biodegradation are not effective as the synthetic dyes are not biodegradable [Robinson et al, 2004; Pearce, 2003]. Methods based on Physical and Chemical process such as chemical oxidation, coagulation, or filtration and membrane separation (Gupta et al., 2006; Han et al., 2007) are costly. The adsorption processes using active carbons are proving to be effective in the removal of dyes from waste waters but they are expensive (Alaton et al, 2008; Ghoreishi and Haghighi, 2003; Tan et al, 2007; Iqbal and Ashiq, 2007). Increasing research interest is being envisaged during the recent past, in exploring the sorption potentialities bio-waste materials of flora and fauna origin in controlling the polluting ions. These bio-processes along with other chemical processes are proving to be potential alternative to the existing methods of detoxification and for the recovery of toxic and valuable ions from industrial discharges/ polluted waters.

These biological approaches have stimulated continuous and expanding research in this field. Fly ash [Mohan et al, 2002], modified calcined diatomite [Khraisheh , 2005], peat [McKay and Allen, 1983], unburned carbon [Wang and Li, 2007], sand [Bakaullah et al, 2007] , Chitosan beads [Cdstari et al , 2008] and plasma treated synthetic polyester fibers have been explored for their efficiency in removing dyes from waste water [Lehocky and Mracek, 2006]. Fertilizer wastes (Srivastava et al., 1997), bentonite clay (Banat et al., 2000; Al. Asheh et al 2003), spent bleaching earths (Pollard et al., 1992), agricultural byproducts (Johns et al., 1998), olive stones (Alaya et al., 2000), and date pits (Banat et al., 2003) have also been probed for their sorption abilities for being used them as bio-sorbents in the pollution control. Our research labs are also making efforts in this aspect of pollution control methods and some successful procedures have been developed for some polluting ions and they have been reported to the Literature [Krishna Veni et al, 2012 a & b; Hanumantha rao et al, 2012 a & b; Divya Jyothi et al, 2012; Suneetha et al, 2012 a & b]. G. Cirini, [2006] reviewed the non conventional low cost adsorbents for dyes.

Some researchers attempted to remove Methylene Blue from waste water using bamboo-based activated carbon [Hameed et al, 2007], gypsum [Mohmmad A Rauf et al, 2009] , treated olive pomace and charcoal [Banat et al, 2010] , activated and non-activated bentonites [Al. Asheh et al, 2003] and water hyacinth [Sachin M Kanawade and Gaikwad, 2011]. But these studies suffer from one or the other disadvantage and a simple, economical, effective and eco-friendly method is still eluding the researchers.

The object of the present work is to probe the plant materials of Tephrosia Purpurea and of Terminalia Arjuna and also the powders of bivalve snail shells for their sorption nature towards Methylene Blue dye from polluted waters. The effect of different process conditions such as pH of the agitating equilibrium, time of equilibration, sorbent dosage and the presence of foreign ions on the % removal of Methylene Blue, have been investigated and the extractions conditions have been optimized.

MATERIALS AND METHODS

(A)CHEMICALS: All chemicals used were of analytical grade.

Stock solution of Methylene Blue: 50 ppm of Methylene blue solution was prepared by dissolving a requisite amount of A.R. grade Methylene Blue dye in double distilled water. It was suitably dilute as per the need.

(B) ADSORBENTS:

While we are exploring the plant materials for their sorption abilities towards the Methylene Blue, it was observed that the adsorbents derived from roots of ***Tephrosia Purpurea, leaves and barks of of Terminalia Arjuna*** and ***bi-valve snail shells*** have shown affinity towards the dye.

A: Tephrosia purpurea ***B: Terminalia Arjuna*** ***C: Bivalves snail shells***

Fig No. 1: Flora or Fauna materials showing affinity towards Methylene Blue dye

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Tephrosia purpurea is a species of flowering plant belongs to Fabaceae family and is a common wasteland weed. It is found throughout India and grows even in poor fertile soils. It has recognized medicinal values and is widely used in Ayrveda in the treatment of leprosy, ulcers, asthma, and tumors. The plant parts are used in curing the diseases of the liver, spleen, heart, and blood. A decoction of the roots is given in dyspepsia, diarrhea, rheumatism, asthma and urinary disorders. The root powder is effective in quickly relieving dental pains and stop bleeding. Terminalia Arjuna is 20-25 meter tall tree belongs to Combretaceae family. It grows on river banks in South Central India. Its leaves are fed to the Antheraea paphia moth which produces the tassar silk, a wild silk of commercial importance. It leaves have shown analgesic and anti-inflammatory properties. Bivalve snail shells have been collected on the sea shore of Suryalanka beach of Bay of Bengal at Bapatla, Guntur District, Andhra Pradesh. The roots of Tephrosia Purpurea and leaves and barks of Terminalia Arjuna were freshly cut from the plants, washed with tap water followed by distilled water and then sun dried. The bi-valve snail shells were washed and dried. All these dried materials were powdered to a fine mesh of size: > 75 microns and activated at 105^{o} C in an oven and then employed in this study.

ADSORPTION EXPERIMENT:

Batch system of extraction procedure was adopted (Trivedy R K., 1995; Gerard Kiely, 1998; Metcalf and Eddy, 2003). Carefully weighted quantities of adsorbents were taken into previously washed 1 lit/500 ml stopper bottles containing 500 ml/250 ml of Methylene Blue solution of predetermined concentrations. The various initial pH values of the suspensions were adjusted with dil HCl or dil NaOH solution using pH meter. The samples were shaken vigorously in mechanical shakers and were allowed to be in equilibrium for the desired time. After the equilibration period, an aliquot of the sample was taken for the determination of Methylene Blue using Spectrophotometric method. The dye has λmax at 661 nm and obeys Beers-Lamber's law at low concentrations. The O.D. measurements were made at the said λmax using UV-Visible Spectrophotometer (Systronics make) (12). The obtained O.D value for un-known solution was referred to standard graphs (drawn between O.D and concentration) prepared with known concentrations of Methylene Blue by adopting method of Least Squares.

The sorption characteristics of the said adsorbents were studied with respect to the time of equilibration, pH and sorbent dosage. At a fixed sorbent concentration, the % removal of Methylene Blue from sample waters was studied varying with respect to the time of equilibration at various pH values. The results obtained were presented in the Graph Nos. A: 1-4. To fix the minimum dosage needed for the maximum removal of the Methylene Blue ions for a particular sorbent at optimum pH and equilibration times, extraction studies were made by studying the % of extraction with respect to the sorbent dosage. The results obtained were presented in the Graph Nos. B: 1.

EFFECT OF OTHER IONS (INTERFERING IONS):

The interfering ions chosen for study were the common ions present in natural waters viz., Sulphate, Fluoride, Chloride, Nitrate, Phosphate, Carbonate, Calcium (II), Magnesium (II), Copper(II), Zinc(II) and Nickel (II). The synthetic mixtures of Methylene Blue and of the foreign ions were so made that the concentration of the foreign ion was maintained at fivefold excess than the dye concentrations as cited in the Table: 1. 500ml of these solutions were taken in stopper bottles and then correctly weighted optimum quantities of the promising adsorbents (as decided by the Graph Nos. A and B) were added. Optimum pH was adjusted with dil. HCl or dil. NaOH using pH meter. The samples were agitated in shaking machines for desired optimum periods and then small portions of the samples were taken out, filtered and analyzed for Methylene Blue concentration. % of extraction was calculated from the data obtained .The results were presented in the Table: 1.

APPLICATIONS OF THE DEVELOPED BIO-SORBENTS:

The procedures developed in this work have been applied for the removal of the dye from real sewage/effluent samples collected from some dyeing industries at Hyderabad and Mangalore. For this purpose, samples were collected from the effluents of industries and the samples were analyzed for the actual amounts of Methylene Blue and then the samples were fed with known amounts of Methylene Blue.

Then these samples were subjected to extraction for the dye using the bio-sorbents developed in this work at optimum conditions of extraction. The results obtained were presented in the Table 2**.**

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RESULTS AND DISCUSSIONS

The extractability of Methylene Blue with the sorbents derived from plant materials of Tephrosia purpurea, Terminalia Arjuna, and Bi-valve snail shells have been studied with respect to various physicochemical parameters such as pH, time of equilibration and sorption concentration and the results obtained are presented in the Graph No. A: 1-4 and Graph No. B: 1. The following observations are significant:

1. Time of equilibration: Percent of extractability increases with time for a fixed adsorbent at a fixed pH and after certain duration, the extractability remains constant, i.e. an equilibrium state has been reached. In other words, there will not be any further adsorption after certain time of equilibration time (vide Graph Nos. A: 1-4). As for example, in the case of powders of leaves of Terminalia Arjuna, % of extraction of Methylene Blue has been found to be 41.1% at 10 min, 67.2% at 20 min, 85.0% at 30 min and 87.0% at 40 min, 88.0% at 50 min, 89.5% at 60 min, 94.5% at 70 min, 98.6% at 80 min and 100% at 90 min or above at pH: 8 or 10.The same trend is found in other sorbents.
2 Effect of pH: The removal of Methylene Blue has been found to be increasing with the increase of pH of the agitating equilibrium for a fixed adsorbent at optimum time of agitation. For example the maximum extractability has been found to be 60.0% at pH: 2; 80.5 % at pH: 4; 91.0% % at pH: 6; 100% at pHs: 8 and 10 after an equilibration period of 90 minutes for the powders of Terminalia Arjuna leaves as sorbent (vide Graph No. A: 2).With the bark powders of Teminalia Arjuna, the % of extraction has been found to be 95.0% at pH: 2; 97.0% at pH: 4; and 100.0 % at pH: 6, 8 and 10 after an equilibration time of 30 minutes (vide Graph No.A:3). Similarly with the root powders of Tephrosia Purpurea, the % of extraction has been found to be 76.1% at pH: 2; 80.2% at pH: 4; 90.1% at pH: 6 and 100.0 % at pH: 8 and 10 after an equilibration time of 120 minutes (vide Graph No.A:1). In the case snail powder, the % of extraction has been found to be 100% at pH range: 12 at 70 min of equilibration with the sorbent concentration 2 gm/500 ml (Graph No. A: 4 and B: 1).
3 Time of equilibration: It is interesting to note that in the case leaves powder of Teminalia Arjuna, the optimum equilibration time need for maximum extraction of Methylene Blue has been found to be 90 minutes at pH: 8 or 10 while with the barks powder of the same plant, the equilibration time has been reduced to 30 minutes. Further, with the bark powders of Terminalia Arjuna, 100% removal of the dye has been found at all pH values except at pH:2 where in the % of extraction has been found to be 95.0%. Incase of root powders of Tephrosia Purpurea and powder of snail shells, the optimum equilibration times have been found to be 120 minutes and 70 minutes respectively at optimum solution pHs.
4 Sorbent Concentration: The optimum sorbent concentration required for the maximum extractability of the Methylene Blue is found to be 2.0 g/500 ml for leaves power of Terminalia Arjuna while with the barks powder, the optimum sorbent concentration has been reduced to 1.5 gm/500 ml. In the case of roots powder of Tephrosia Purpurea , the optimum sorbent concentration has been found to be only 1.0 gm/500 ml. Thus roots powder of Tephrosia Purpurea has been proved to very effective as 1.0 gm/500 ml of it is sufficient to remove completely the Methylene Blue at the optimum conditions of pH:8 or 10 and 120 minutes of equilibration. With snail powder, the optimum sorbent concentration has been found to be 2.0 gm /500 ml. (vide Graph No. B: 1).
5 Interfering Ions: The extractability of Methylene Blue in presence of fivefold excess of common ions found in natural waters, namely, Sulphate, Phosphate, Chloride, Carbonate, Fluoride, Calcium, Copper, Iron, Zinc and Magnesium ions, has been studied. The results are presented in Table No.1.
   - Anions envisaged marginal effect on the % extractability of Methylene Blue with the sorbents of the present work at the optimum conditions of time of equilibration, pH and sorbent concentration.
   - Cations like Fe^{2+} and Zn^{2+} have not interfered and synergistically maintained the maximum% of extraction while cations like Ca^{2+}, Mg^{2+} and Cu^{2+} have interfered to a less extent with the % of extraction of the dye.

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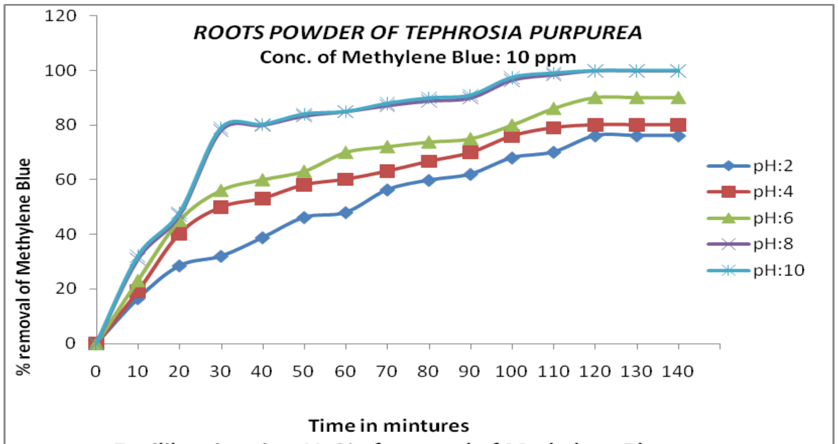
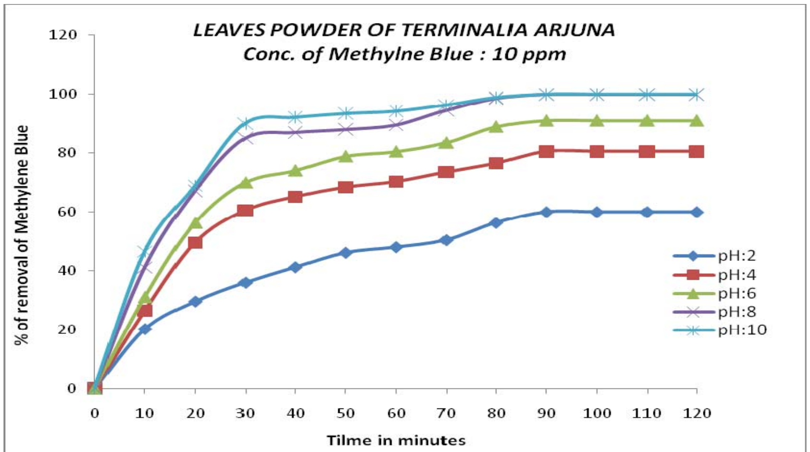


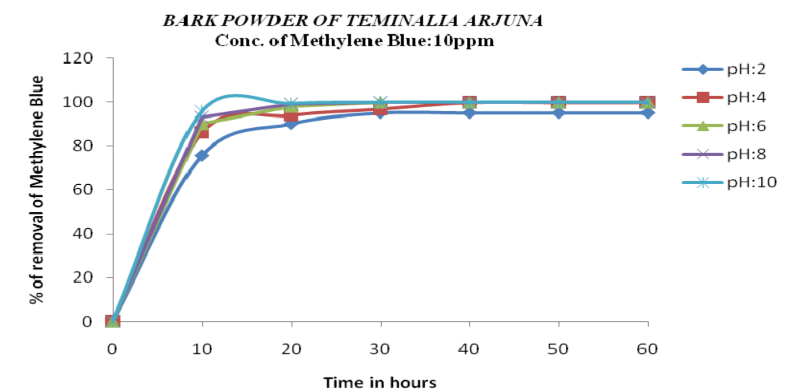
Equilibration time Vs % of removal of Methylene Blue

Graph No. A: 1



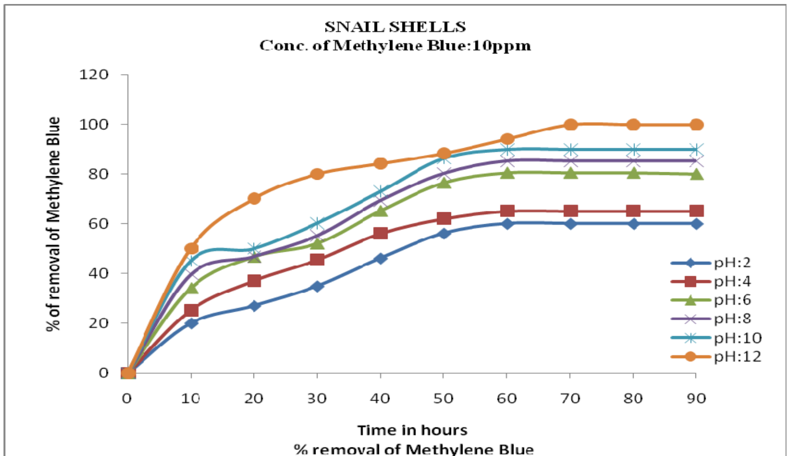
Equilibration time Vs % of removal of Methylene Blue

Graph No. A:2

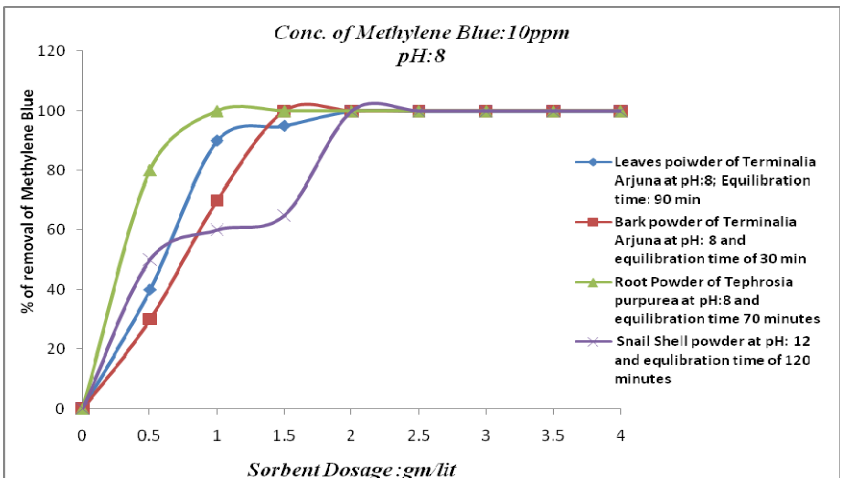


Equlibration time Vs % removal of Methylene Blue

G raph No: A: 3



% removal of Methylene Blue
Graph No: A:4



Sorbent Dosage Vs % removal of Methylene Blue
Graph No:B-1

Table No. :1: Effect of interfering Ions on the Extractability of Methylene Blue with different Bio-sorbents

dsorbent and its concentration	Maximum Extractability at optimum conditions	*Extractability of Methylene Blue in presence of fivefold excess of (50 ppm) interfering ions at optimum conditions: Conc of Methylene Blue: 10 ppm*									
		SO_4^{2-}	PO_4^{3-}	Cl^-	CO_3^{2-}	F^-	Ca^{2+}	Cu^{2+}	Fe^{2+}	Zn^{2+}	Mg^{2+}
Root powders of Tephrosia Purpurea	100.0%; pH: 8 or 10; Agitation time: 120 min; sorbent conc.: 1.0 g/500 ml	98.0%	98.5%	98.0%	100. 0%	98.5%	93.4%	925%	100.0%	100.0%	94.0%
Leaves powder of *Terminalia Arjuna*	100.0%; pH:8 or 10; Agitation time: 90 min; sorbent conc.: 2.0 g/500 ml	99.5%	99.0%	97.8%	99.7%	97.5%	92.0%	93.3%	100.0%	100.0%	95.6%
Stems powder of *Terminalia Arjuna*	100.0%; pH:8 or 10; Agitation time: 30 min; Sorbent conc.:1.0 g/1500 ml	100.0%	99.2%	98.9%	100. 0%	99.2%	91.5%	94.5%	100.0%	100.0%	96.5%
Bivalve snail shells powder	100.0%;pH:12 ; Agitation time: 70 min ; Sorbent conc.: 2.0 g/500 ml	99.0%	99.5%	99.8%	100.0%	97.9%	95.0%	93.9%	100.0%	98.5%	94.0%

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DISCUSSIONS

The available data is in adequate to account theoretically each observation made as it needs surface studies to understand the sorption chemistry using such modern instruments like X-ray Photo Electron Spectroscopy (XPS), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS) techniques in addition to the classical elemental chemical analysis before and after the sorption of the adsorbate on the sorbent surface and it is beyond the aims of this work.

However, the observations may be accounted as follows:

- The bio-sorbents derived from roots, leaves and barks have -OH/COOH groups and their dissociation is pH dependent and this imparts weak anion exchange ability at low pH values and weak cation exchange ability at high pH values as per the equilibrations:

At high pH values: Adsorbent-OH $\rightleftharpoons$ Adsorbent-O^- + H^+
Adsorbent-COOH $\rightleftharpoons$ Adsorbent-COO^- + H^+

At low pH values: Adsorbent-OH + H^+ $\rightleftharpoons$ Adsorbent-O^+H
H

- Methylene Blue being a cationic in nature is sorbed by these plant materials at high pHs due to weak cation exchange nature and thus results in higher % of removal at high pH values. As pH decreases, the cation exchanging nature decreases and this results in gradual decrease in % removal of Methylne Blue dye.

- Snail shells are chemically Calcium carbonates to an extent of 97.5% and the reset is calcium phosphate and silicate, magnesium carbonate and oxide, iron and manganese oxide and other organic substances (Aboua, 1995). At high values, negative charges prevail on the surface of the finally ground powder (Jatto, 2010) and these charges impart thrust for cations. Methylene Blue being a cation, shows affinity towards the sorbent and hence the observed behavior of increase in extractability with the increase in pH.

- The decrease in the rate of adsorption with the progress in the equilibration time may be due to the more availability of adsorption sites initially and are progressively used up with time due to the formation of adsorbate film on the active sites of adsorbent and thus resulting in decrease in capability of the adsorbent.

- The observations made with respect to the foreign ions are also confirming as per the expected nature of extraction. The negatively charged surface at the high pH values show less affinity towards anions and so, % of extractability is not affected even in the presence of fivefold excess of anions chosen for study. But, some cations like Ca^{2+}, Mg^{2+} and Cu^{2+}compete with methelene blue for sorption sites on the sorbents resulting some inference. But this is not found in the case of Zn^{2+} and Fe^{2+} because the Zn^{2+} ion forms negatively charged zincate at the high pH resulting no affinity towards the sorbent while Fe^{2+} gets precipitated as ferrous hydroxide at high pH and thus resulting precipitate also adsorbs or traps the methylene dye effecting the complete removal of Methylene Blue dye from the samples.

APPLICATIONS

The Applicability of the methodologies developed in this work have been tested with respects to the real samples of diverse nature, collected from the sewages/effluents of dyeing industries which are fed with varying quantities of the dye :Methylene Blue. The results have been presented in the Table No: 2.

Table No. 2: % of Extractability of Methylene Blue from different industrial effluents with bio-sorbents developed in this work

Bio-Sorbent	% of Extractability of Methylene Blue				
	Sample 1: Fed with 10.0 ppm of Methlene Blue	Sample 2: Fed with 15.0 ppm of Methlene Blue	Sample 3: Fed with 20.0 ppm of Methlene Blue	Sample 4: Fed with 25.0 ppm of Methlene Blue	Sample 5: Fed with 30.0 ppm of Methlene Blue
Root powders of Tephrosia Purpurea :at pH:8; Equilibration time: 120 min and sorbent concentration: 1.0 g/500 ml	93.0%	92.5%	96.0%	95.5%	94.9%
Leaves powder of ***Terminalia Arjuna***: at pH:8; Equilibration time: 90 min and sorbent concentration: 2.0g/500 ml	92.9%	91.5%	94.5%	95.5%	92.5%
Stems powder of ***Terminalia Arjuna***:at pH:8; Equilibration time: 30 min and sorbent concentration: 1.5 gms/500 ml	96.5%	95.6%	94.0%	92.5%	93.5%
Bivalve snail shells powder :at pH:12 ; Equilibration time: 70 min and sorbent concentration: 2.0 gm/500 ml	97.0%	94.5%	95.3%	94.3%	93.8%

It is found that the sorbents developed in this work are successful in removing Methylene Blue at optimum conditions of pH, equilibration time and sorbent dosage as cited in the Table No.2. Percentage of removal of Methylene Blue is found to be between: 92.5% to 100% with leaves powder of Terminalia Arjuna; 93.5% to 100.0% with stems powder of Teminalia Arjuna; 91.5% to 100.0% with root powders of Tephrosia Purpurea and 92.0% to 100.0 % with Bivalve snail shells powder.

CONCLUSSIONS

1. Sorbents derived from roots of Tephrosia Purpurea, leaves and stems of Terminalia Arjuna and Bivalve snail shells have been found to have strong affinity towards Methylene Blue at high pH values.
2. The conditions of extraction namely, pH, sorbent concentration and time of equilibration for the maximum removal of Methylene Blue from waste, have been optimized.
6 Optimum equilibration time is found to be 90 minutes for the leaves powders of Terminalia Arjuna while with the barks powder the equilibration has been reduced to 30 minutes. In case of root powders of Tephrosia Purpurea and powder of snail shells, the optimum equilibration time has been found to be 70 minutes and 120 minutes respectively.
7 Sorbent Concentration is found to be 2.0 g/500 ml for leaves power of Terminalia Arjuna and 1.5 gm/500 ml. with its bark powders. The roots powder of Tephrosia Purpurea has been proved to very effective even at the 1.0 gm/500 ml of the sorption concentration.The optimum concentration is found to be 2.0 gm/500 with snail powders.
3. It is interesting to note that more than 95.0% of extraction of Methylene Blue has been found with the bark powders of Terminalia Arjuna at all pH of study viz., 2-10.
4. Fivefold excess of common anions ions present in natural waters, have not interfered the extractability of Methylene Blue at optimum extraction conditions. Cation like Ca^{2+}, Mg^{2+} and Cu^{2+} have shown some interference but while Fe^{2+} and Zn^{2+} have synergistically maintained the maximum extraction of the dye.
5. Successful methodologies have been developed for the complete removal of Methylene Blue dye from synthetically prepared waste waters with the bio-sorbents under study.
6. The procedures have been found to be remarkably successful in removing the Methylene Blue from industrial effluents as detailed in Table No: 2.

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REFERENCES

Aboua , F.(1995). Proximate Analysis and Mineral contents of two giant African snails consumed in IvoryCoast, Tropical science, England.

Al. Asheh, S., F. Banat L. Abu-Aitah (2003). "The removal of methylene blue dye from aqueous solutions using activated and non-activated bentonites". Ads. Sci.Tech, 21, 451-462.

Alaton,I. A., B. H. Gurso , J. E. Schmidt (2008). "Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes", Dyes Pigm , 78,117-130.

Albanis, V., Dhanjal, S., MacDonald, K., Petropoulos, P., Offerhaus, H.L., Richardson, D.J., Rode, A., Zheludev, N.I., 1988. The light induced structural phase transition in confining gallium and its photonic applications. Journal of Luminescence 87–89, 646–648.

Alaya, M.N., Hourieh, M.A., Youssef, A.M., El-Sejariah, F., 2000. Adsorption properties of activated carbons prepared from olive stones by chemical and physical activation. Adsorption Science and Technology 16, 27–42.

Bakaullah, S.B. M. A. Rauf ,S .S. AlAli (2007). "Removal of Methylene Blue from aqueous solution by adsorption on sand", Dyes Pigm., 74, 85-87.

Banat, I. M., P. Nigam, D. Singh, R. Marchant (1996). "Microbial decolorization of textile-dye-containing effluents: a review". Biores. Tech., 58, 217–227.

Banat, F., Al-Bashir, B., Al-Asheh, S., Hayajneh, O. (2000). "Adsorption of phenol by bentonite", Environmental Pollution 107, 391–398.

Banat, F., S. Al-Asheh, R. Al-Ahmad, F. Bni-Khalid (2010). "Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal", Iran. J. Environ. Health. Sci. Eng., 7, 5, 423-428.

Boeningo, M., "Carcinogenicity and metabolism of azodyes especially derived from benzidine". Washington DC, U.S Gov. Printing Off; DNHS(NIOSH) publication, July 1994,. 80-119.

Cestari , A.R., E. F. S. Viera , J. A. Mota(2008). "The removal of an anionic red dye from aqueous solutions using chitosan beads-The role of experimental factors on adsorption using a full factorial design", J.Hazard. Mat., 160, 337-343.

Cirini, G. (2006). "Non conventional low cost adsorbents for dye removal: A review", Biores. Tech., 589. 67-75.

Divya Jyothi, M., K Rohini Kiran , K Ravindhranath (2012). "Phosphate pollution control in waste waters using new bio-sorbents", International Journal of Water Resources and Environmental Engineering, 4(4), 73-85.

Gerard Kiely, Environmental Engineering, McGraw-hall International Editions. 1998.

Ghoreishi, S.M., R Haghighi (2003). "Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent". Chem.Eng.J, 95, 163-169.

Gupta, V. K., Mittal, A., Krishnan, L., Mittal, J.,(2006). J. Colloid Interface Sci. *293:16.*

Hameed, H., A. T. M. Din , A. L. Ahmed (2007). "Adsorption of Methylene Blue onto bamboo-based activated carbon: kinetics and equilibrium studies", J.Hazard. Mat., 141, 819-825.

Han, R., Wang, Y., Zou, W., Wang, Y., Shi, J., (2007). J. Hazard. Mater. 145:331.

Hanumantha Rao, Y., Medikondu Kishore, K. Ravindhranth (2012). "Characterization And Defluoridation Studies Using Activated Acacia Farnesiana Carbon As Adsorbent", Electronic Journal of Environmental, Agricultural and Food Chemistry, 2012, 11(5) :442-458. [25] B.

Hanumantha Rao, Y., Medikondu Kishore, K Ravindhranath (2012). "Characterization And Defluoridation Studies Of Active Carbon Derived From Typha Angustata Plants", Journal of Analytical Science and Technology (in press)

Ho, Y. S., McKay, G., (1998). The kinetic of sorption of basic dyes from aqueous solution by sphagnum Moss peat. Can. J. Chem. Eng. 76: 822.

Iqbal , M.J., M. N. Ashiq (2007). "Adsorption of dyes from aqueous solutions on activated charcoal", J.Hazard. Mat., 139, 57-66.

Jatto, E.O., I.O Asia1, E.E Egbon, J.O Otutu, M.E Chukwuedo , C.J Ewansiha (2010). "Treatment Of Waste Water From Food Industry Using Snail Shell", Acaedmia Arena 2(1), 32-36.

Johns, M.M., Marshall, W.E., Toles, C.A., 1998. Agricultural by-products as granular activated carbons for adsorbing dissolved metals and organics. Journal of Chemical Technology and Biotechnology 71, 131–140

Khraisheh, M. A., M. S.Alg-Houti (2005). "Enhanced Dye Adsorption by Microemulsion Modified Calcined Diatomite (E-CD)". Ads. 11, 547-549.

Krishna Veni, V., K. Ravindhranath (2012). "Extraction of Chromium (VI) from Waste Waters Using Powders and Their Ashes of Barks of Ficus benghalensis, Tamarindus indica and Acasia niloticaIndica", Asian J. Research Chem., 5(2), 225-233.

Krishna Veni, V., K. Ravindhranath(2012). "Chromium (VI) pollution control in waste waters using new bio-sorbents", 2012, 7(2), 67-80.

Lehocky, M., A. Mracek (2006). "Improvement of dye adsorption on synthetic polyester fibers by low temperature plasma pre-treatment", Czech. J. Phy., 2006, 56, 1277-1282.

McKay, G., S. J. Allen (1983). "Single resistance mass transfer models for the adsorption of dyes on peat". J.Sep. Proc.Tech., 4, 1-7.

Metcalf and Eddy. Wastewater Engineering: Treatment of Reuse. 4th. Ed, New York: McGraw Hill Co. 2003.

Mohan, D., K. P. Singh, G. Singh, K Kumar (2002). "Removal of dyes from wastewater using flyash, a low cost adsorbent". Ind. Eng. Chem. Res., 41, 3688-3695.

Muhammad A Rauf, I. Shehadeh, Amal Ahmed, Ahmed Al-Zamly (2009). "Removal of Methylene Blue from Aqueous Solution by Using Gypsum as a Low Cost Adsorbent", World Academy of Science, Engineering and Technology, 2009, 55, 608-613.

Pearce, C. I., J. R. Lloyd, J. T. Guthrie (2003). "The removal of colour from textile wastewater using whole bacterial cells: a review". Dyes Pigm., 58, 179-196.

Pollard, S.J.T., Fowler, G.D., Sollars, C.J., Perry, R., 1992. Low-cost adsorbents for waste and wastewater treatment: a review. The Science of The Total Environment 116, 31–52.

Robinson, T., G. McMullan, R. Marchant, P. Nigam (2004). "Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative". Bioreso. Tech., 77, 247–255.

Sachin M Kanawade, R. W. Gaikwad (2011). "Removal of Methylene Blue from Effluent by Using Activated Carbon and Water Hyacinth as Adsorbent" International Journal of Chemical Engineering and Applications, October, 2 , 5, 317-319.

Srivastava, K., Tyagi, R., Pal, N., Mohan, D., 1997. Nanofiltration of textile wastewater for water reuse. Journal of Environmental of Environmental 143, 11–20

Stydini, M., Dimitris, I. K., Verykios, X. E., (2004). Visible light-enduced photocatalytic degradation of acid orange 7 in aqueous TiO2 suspensions. Appl. Catal. Environ. 47:189.

Suneetha, M., K Ravindhranath (2012). "New bio-sorbents in controlling ammonia pollution in wastewaters", Journal of Chemical and Pharmaceutical Research, 4(1):526-537.

Suneetha, M.,, K . Ravindhranath (2012). "Removal of Nitrite from Polluted Waters using Bio-sorbents derived from Powders of Leaves, Barks or Stems of Some Herbal Plants", International Journal of Chemical, Environmental and Pharmaceutical Research, 3(1), 24-34.

Tan, I.A.W., B. H. Hameed , A. L. Ahmad (2007). "Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon", Chem. Eng. J., 127, 111-119.

Trivedy R.K., "Pollution Management in Industries" 2nd ed. Karad (India): Environmental Publications; 1995.

Walker, G. M., Hansen, L., Hanna, J. A., Allen, S. J., (2003). Kinetics of a reactive dye adsorption onto dolomitic sorbents. Water Res. 37: 2081.

Wang , S., H. Li (2007). "Kinetic modelling and mechanism of dye adsorption on unburned carbon", Dyes Pigm., 72, 308-14.