

Research Article

Adsorption potential of *Euphorbia Hirta*'s (leaf and bark) towards methyl red in aqueous systems

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Abstract

Dyes harm both aquatic species and humans in wastewaters, which are poisonous as well as carcinogenic. For decades, the adsorption system technique has been widely used to take out dyes from aqueous solutions since it is a trouble-free and successful process. The present study investigated the use of *Euphorbia hirta*'s leaf powder/bark powder/leaf ash/bark ash for the adsorption of methyl red dye (MRD) from aqueous samples for the first time. MRD aqueous solutions (250 ml, 100 ppm) were incubated for the required contact period with 1.2 gm/l of investigated sorbent with agitation at 100 rpm. The temperature and pH remained maintained at 27 degrees Celsius and 4.0, respectively. The residual amounts of MRD were evaluated by spectro-photometrically measuring MRD absorbance at 464.9 nm. The percent MRD clearance using *E. hirta*'s leaf powder/bark pow-der/leaf ash/bark ash showed that the optimal condition of MRD clearance happened at pH unit of 4, 100 ppm concentration of MRD, sorbent dose at 1.2 gm/l, ambient temperature, mechanical shaker agitation speed of 100 rpm. The optimal equilibration time for highest percentile MRD clearance was 125 min (*E. hirta* leaf powder), 105 min (*E. hirta* leaf ash powder and *E. hirta* bark powder) and 90 min (*E. hirta* bark ash powder). Negatively charged chemical groups like –COOH, -CHO, -NH, etc. present in the phytochemicals of *E. hirta*'s leaf and stem binds to positively charged ions in MRD, as a result, adsorption occurs. For its significant biosorption potential and cheap cost, *E. hirta*'s leaf powder/bark powder/leaf ash/bark ash can be regarded as alternative biomass for removing MRD from the aqueous solution.

Keywords: Aqueous system, Biosorbent, Biosorption, Euphorbia hirta, Spectroscopic analysis

INTRODUCTION

In recent times, accelerated advancement in industrial operations has resulted in the release of an unprecedented volume of wastewater with artificial dyes that contaminate waterways and, as a result, affect humans and other living species (De Luca and Nagy, 2020). A large percentage of the colours utilised are azo reactive dyes (Benkhaya *et al.*, 2020). Because one or more azo groups are coupled with substituted aromatic structures, those dyes have a brilliant colour (Forgacs *et al.*, 2004). Textile, cosmetics, foods processing, leather, paper and dye industry effluents are only a few examples of discharged azo dyes (Bhatnagar and Jain, 2005). Living creatures are poisoned by these colours or their breakdown products (Chung *et al.*, 1981). Colorants in wastewater are very challenging to eliminate since they are light, heat, and oxidising agent resistant. In a nutshell, they are difficult to deteriorate (Jain and Sikarwar, 2008). To accomplish a high degree of removal of dye in wastewater systems, chemical, biological, & physical procedures like coagulation, ultrafiltration, electro-chemical adsorption, & photooxidation must be integrated (Kargi and Ozmihci,

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2004). Because of their great effectiveness and capacity to segregate a broad range of chemical components, physical adsorption methods are typically chosen as the ideal approach to removing/purifying organic pollutants (Imamura *et al.*, 2002; Ho *et al.*, 2003; Ofomaja and Ho, 2006; Kokkiligadda *et al.*, 2020).

Owing to the minimal price and broad availability of agricultural residues as starting resources, their use has sparked a lot of research interest. Palm kernel fibres (Ofomaja, 2007), sugarcane bagasse (Azahar *et al.*, 2005), peel of banana (Annadurai *et al.*, 2002), barn of rice and wheat (Xue *et al.*, 2008), rice husk (Lakshmi *et al.*, 2009), tea waste (Tamez *et al.*, 2009; Indolean *et al.*, 2017), shell of coconut (Singh *et al.*, 2008), apple pomace and wheat straw (Robinson *et al.*, 2002), garlic peel (Hameed and Ahmad, 2009), almond shells (Loulidi *et al.*, 2020), Eucalyptus globulus seeds (Renita *et al.*, 2021), flower spikes (Parlayıcı and Pehlivan, 2021) are examples of agro wastes that have been utilised to remove colours.

A pantropical weed, *E. hirta*, occasionally named asthma-plant, originated from tropical regions (Kumar *et al.*, 2010) is a hairy herb growing on roadsides, open grasslands, also in pathways. Several cultures employ it in classic herbal therapy, especially for asthma, skin problems, & hypertension (Xia *et al.*, 2018). It is also used as a folk medicine treating fevers, especially dengue fever & malaria, in the form of herbal tea (Perera *et al.*, 2018; Shah *et al.*, 2019). This herb has never been used to eliminate methyl red dye (MRD) from contaminated water as a biosorbent.

As a result, the primary goal of this research was to determine whether *E. hirta*'s leaves powder, leaves ash, bark powder, and bark ash could be used to build a unique sorbent and also to test its efficacy in eliminating MRD from simulated wastewater. The related factors, including pH, sorbent dose, and contact time, were evaluated systematically.

MATERIALS AND METHODS

Sorbent

Euphorbia hirta, a member of the Euphorbiaceae family, was available locally. The *E. hirta* plant's leaves and barks were selected, chopped into small pieces, cleaned with double-distilled water, and sun-dried for seven days. The dried leaves/dried bark were pulverised in a high-powered blender and subsequently sieved to get rid of the fibres. The dried leaves/bark were burned in a furnace for a nearly two-hour time period to make the *E. hirta* leaf ash/bark ash.

Adsorbate-methyl red

"Merck India Ltd, India" provided the methyl red, which was utilised without additional purification. For this investigation, a methyl red dye (MRD) solution with a content value of 100 ppm was prepared. The produced MRD solution was covered using aluminium foil and preserved in the dark to avoid unnecessary light exposures.

Adsorption experiments

The sorbents (E. hirta's leaf powder/bark powder/ leaf ash/bark ash) were precisely weighed and placed in previously cleansed 500 mL capped bottles holding 250 mL of MRD (100 ppm quantity) solution. The pH of the mixtures (sorbent + MRD solution) was adjusted using HCl of 0.1 M strength or NaOH of 0.1 M strength solutions, depending on their starting pH values. Mechanical mixers were used to vigorously shake the mixtures (sorbent + MRD solution), which were then allowed to equilibrate for the necessary duration of time. However, after the equilibration time, an aliquot of the mixture (sorbent + MRD solution) was collected for the Spectrophotometric measurement of MRD remaining in mixture. The MRD obeys "Beer-Lamberts Law" at trace concentrations and has a maximum wavelength of 464.9 nm. The MRD absorbance measures were recorded at 464.9 nm with a UV-Visible spectrophotometer fabricated by "Systronics" company. From MRD absorbance measures, remaining content (ppm) of MRD can be gauged.

The following formulae were used to compute the percent of MRD removed (%) and the quantity of MRD adsorbed (mg/gm).

Percent of MRD removed (%)= MRD IC-MRD EC/ MRD IC X 100Eq.1 Quantity of MRD absorbed (qe) = MRD IC-MRD EC/ AS X VEq.2 Where MRD IC means MRD initial concentration (mg/ L); MRD EC means MRD equilibrium concentration (mg/l); AS means sorbents (*E. hirta*'s leaf powder/bark powder/ leaf ash/bark ash) mass; and V means test MRD solution (I).

The % clearance of MRD from simulated water specimens was investigated using the above-mentioned experimental approach regarding time of equilibration, pH values, agitation speed of mechanical shaker, temperature, initial MRD quantity, and sorbent dosage concentration.

RESULTS AND DISCUSSION

Methyl Red Dye (MRD) is a ubiquitous mono azo dye in use in laboratory assays, textile, as well as other business items. Nevertheless, it can induce eye and skin sensitivities and pharyngeal and digestive system discomfort (Shilpa *et al.*, 2013; Maniyam *et al.*, 2020). MRD is also mutagenic at aerobic conditions, as it biotransforms to 2-aminobenzoic acid & N-N' dimethyl-pphenylene diamine (Vijaya and Sandhya, 2003; Jadhav *et al.*, 2008). Recently, there has been a surge in interest in devising low-cost methods for lowering, if not totally eliminating, MRD present in wastewater prior to its disposal into receiving water.

Phytochemical investigation of E. hirta's leaves and stems by a number of investigators (Basma et al., 2011; Singh and Kumar, 2013; Kumar et al., 2010) shows the existence of phytochemicals like 1,3,4,6tetra-O-galloyl-β-D-glucose, 24-methylenecycloartenol, 2,4,6-tri-O-galloyl-β-D-glucose, 24-methylenecycloartenol, afzelin, alkaloids, camphol, choline, chtolphenolic acid, euphorbins type A - D, flavonoids, gallic acid, heptacosane, kaempferol, myricitrin, nnonacosane, protocatechuic acid, quercitrin, reducing sugars, rhamnose, rutin, shikmic acid, steroids, tannins, terpenoids, tinyatoxin, β-amyrin and β-sitosterol. Functional groups like as -COOH, -CHO, -NH, etc. are found in above said phytochemicals. Adsorption occurs when these negatively charged chemical groups in adsorbents bind positively charged ions in MRD.

Equilibration time

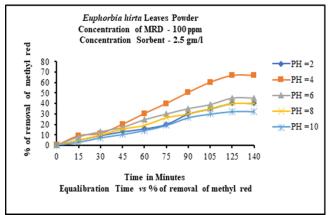
The present study observed that for a given sorbent (*E. hirta*'s leaf powder/bark powder/ leaf ash/bark ash) at a given pH, the % clearance of MRD improves over time, and after a particular period of time, the % clearance of MRD kept static, indicating that an equilibrium point has indeed been established. Fig. 1-4 represent the findings. At a 125-minute equilibration time, the greatest

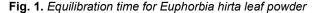
percentile clearance of MRD was achieved with *E. hirta* leaf powder (Fig. 1). The equilibration time was 105 min with *E. hirta* leaf ash powder (Fig. 2) and *E. hirta*'s bark powder (Fig. 3). The greatest percentile clearance of MRD was achieved at an equilibration time of 90 min with *E. hirta*'s bark ash powder (Fig. 4).

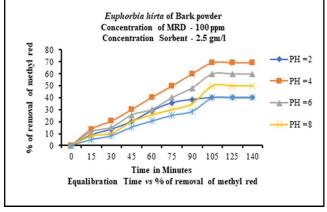
As compared to earlier research, Kadam *et al.* (2018) found that plants (*Ammannia baccifera and Fimbristylis dichotoma*) had cleared MRD up to 89% and 91% later 60 h of exposure, respectively. According to Chandanshive *et al.* (2016) *Salvinia molesta* was shown to be capable of degrading azo dye up to 97% in 3 days utilising root biomass.

Percentage clearance of MRD by sorbents as a function of pH

Owing of its impact on the surface character traits of the sorbents (*E. hirta*'s leaf powder/bark powder/leaf ash/bark ash) and the dissociation/ionization of the MRD molecule, the pH of the reaction has a significant influence on MRD molecule adsorptive uptake. Using a starting concentration of MRD (100 ppm) around 250 mL and 2 g of sorbent (*Euphorbia hirta*'s leaf powder/ bark powder/ leaf ash/bark ash), the impact of pH on % clearance of MRD was evaluated. The pH of the mixtures (sorbent + MRD solution) was adjusted using HCI of 0.1 M strength or NaOH of 0.1 M strength solutions









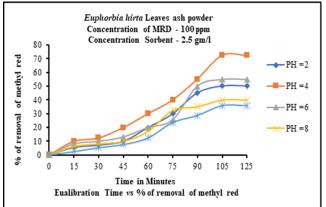


Fig. 2. Equilibration time for Euphorbia hirta leaf ash powder

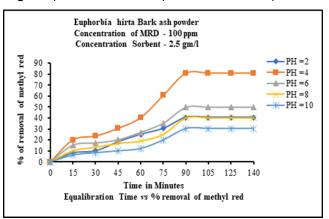


Fig. 4. Equilibration time for Euphorbia hirta bark ash powder

depending on their starting pH units to form a sequence of pH units 2, 4, 6, 8 and 10. Mechanical shakers adopted to agitate the suspensions at ambient temperature showed that the % clearance of MRD in solutions with diverse pH units (2, 4, 6, 8 and 10) is made known in Table 1. The % MRD clearance capacity of investigated sorbents (E. hirta's leaf powder/bark powder/leaf ash/bark ash) improved from pH units 2 to pH 4 and diminished from 6 to 10 pH units. Maximum % MRD clearance was attained at pH unit 4 for all investigated sorbents (E. hirta's leaf powder/bark powder/ leaf ash/ bark ash). Low pH (2–4) causes a rise in H⁺ ions intensity in the chemical system. The surfaces of the sorbents (E. hirta's leaf powder/bark powder/ leaf ash/ bark ash) obtained a positive charge by accepting H^{+} ions. This increases the sorbent's adsorption capability and hence the % MRD clearance. The adsorption efficiency of these sorbents (E. hirta's leaf powder/bark powder/leaf ash/bark ash) was reduced at excessive pH units (6 to 10) because MRD's loss of H⁺ ions rendered it negatively charged and unable to engage with the investigated sorbents. The current study's findings are comparable to those of Krishna et al. (2020). Krishna et al., 2020) reported the optimized pH value of 4 for maximum MRD clearance by Charred Sal sawdust and Xanthated Sal sawdust.

Effects of considered sorbents dose on percentage MRD clearance

The effect of investigated sorbents (*E. hirta*'s leaf powder/bark powder/leaf ash/bark ash) dose on the percentage MRD clearance with optimum MRD concentration (100 ppm) at 250 mL was inspected with sorbent doses of 0.2 gm/l, 0.4 gm/l, 0.6 gm/l, 0.8 gm/l, 1.0 gm/l, 1.2 gm/l and 1.4 gm/l. The pH of the mixtures (sorbent + MRD solution) was adjusted using HCl of 0.1 M strength or NaOH of 0.1 M strength solutions to 4 pH. Mechanical shakers were adopted to agitate the suspensions at ambient temperature, and the % clearance of MRD was evaluated at corresponding equilibration times of investigated sorbents. The % clearance of MRD in solutions with diverse dose quantities of investigated sorbents is made known in Table 2. The percentage MRD clearance capacity of investigated sorbents increased from dose quantities 0.1 to 1.2 gm/l at corresponding equilibration times and pH of 4 units. The percentage MRD clearance capacity constantly persisted from 1.2 gm/l dose quantities. As compared to earlier research, Kaya (2017) found that 4 gm dose each of walnut shell and hazelnut shell had cleared 79% and 77% MRD, respectively. Vatsal (2017) reported that 4 gm to 5 gm of orange peel powder is the optimum amount for maximum MRD clearance.

Percentage clearance of MRD by sorbents as a function of temperature

Table 3 shows the percentile MRD clearance by researched sorbents (*E. hirta*'s leaf powder/bark powder/ leaf ash/bark ash) versus ambient, 40 °C, 50 °C, and 60 °C temperatures. The quantities of dye adsorbed by the examined sorbents (*E. hirta*'s leaf powder/bark powder/ leaf ash/bark ash) remained consistent as the temperature increased, as indicated. As a result, an ideal ambient temperature of 27 °C was chosen. Our findings are consistent with those of Eman's previous research (2020). Whereas Sunil *et al.*, discovered that increasing the temperature from 25°C to 55°C improved the proportion of MRD removed by eggshell waste.

 Table 1. Percentage clearance of MRD by investigated sorbents as a function of pH

pH unit	% MRD clearance with <i>E. hirta</i> 's				
	Leaf powder	Bark powder	Leaf ash	Bark ash	
2	40.2	40.5	50	53	
4	65.8	69.5	65	60	
6	44.8	44	45	48	
8	40.1	32	30	40	
10	30.4	21	25	35	

Table 2. Percentage clearance of MRD by investigated sorbents as a function of dose quantity

Dooo guantity (gm/l)	% MRD clearance with <i>E. hirta</i> 's				
Dose quantity (gm/l)	Leaf powder	Bark powder	Leaf ash	Bark ash	
0.2	30.5	30	31	28	
0.4	40.9	40.6	48	46	
0.6	51.2	45.8	57	61	
0.8	63.7	58.7	69	68	
1.0	72	70.2	78	74	
1.2	88.2	78.2	91	90	
1.4	88.2	78.2	91	90	

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Carbont	Percentile MRD clearance at temperature of				
Sorbent	Ambient		40 °C	50 °C	60 °C
Leaf powder	81.6		81.5	81.4	81.6
Leaf ash	82.4		82.4	82.3	82.4
Bark powder	87.2		87.1	87.1	87.1
Bark ash	82.5		82.3	82.5	82.4
Table 4. Percentile	MRD clearance at diverse	e initial MRD qua	intity		
Sorbent	Percentile MRD clearance at initial quantity of MRD at				
Sorbeni	100 ppm	150 ppm	200 ppm	250 ppm	300 ppm
Leaf powder	86.4	74.8	72.6	65.4	64.1
Leaf ash	90.2	85.4	62.1	60.4	59.7
Bark powder	85.6	81.2	79.6	70.5	69.7
Bark ash	88.9	79.2	75.8	69.1	66.8
Table 5. Percentile	MRD clearance at divers	e agitation speed	ds		
Sorbent	Percentile MRD clearance at initial quantity of MRD at				
Solbent	50 rpm	100 rpm	150 rpm	200 rpm	250 rpm
Leaf powder	87.5	91.6	90.4	85.6	71.5
Leaf ash	83.5	96.4	95.7	92.5	84.3
Bark powder	89.6	95.2	91.0	83.4	79.4

94.8

Table 3. Percentile MRD clearance at diverse temperature

Effect of MRD initial quantity on percentage MRD clearance by considered sorbents

91.6

Bark ash

A 1.2 gm/l sorbents (Euphorbia hirta's leaf powder/ bark powder/leaf ash/bark ash) included in MRD solutions with different dye quantities (100 ppm, 150 ppm, 200 ppm, 250 ppm and 300 ppm) showed that the pH of the solution (sorbent + MRD) was retained at 4 and the solution (sorbent + MRD) was agitated for optimal equilibration time. Table 4 demonstrates the relationship between the MRD amount cleared and the initial quantity of MRD in the solution. The MRD elimination % was shown to be lower the greater the initial MRD concentration. The adsorbent's surface has a substantial percentage of unoccupied sites at the beginning of the adsorption activity (Munir et al., 2020; Sintakindi and Ankamwar, 2020). The proportion of such sites diminishes as the adsorption mechanism progresses. There are plenty of active sites on the sorbent's surface with low initial MRD concentrations. However, there is just not enough empty active sites at high initial MRD concentrations. According to Noha et al. (2020), when the starting MRD concentration increased from 10 to 100 ppm, the percentage elimination of MRD dropped with oil shale.

Effect of agitation speed on percentage MRD clearance by considered sorbents

The consequence of agitation speediness on the percentage MRD clearance with optimum initial MRD concentration (100 ppm) at 250 mL with sorbents dose of 1.2 gm/l showed that the pH of the solution (sorbent + MRD) was retained at 4. Mechanical shakers were adopted to agitate the suspensions at diverse agitation speeds like 50 rpm, 100 rpm, 150 rpm, 200 rpm, and 250 rpm. The % clearance of MRD was evaluated at corresponding equilibration times (125 min - E. hirta's leaf powder; 105 min - E. hirta's leaf ash powder and E. hirta's bark powder; 90 min - E. hirta's bark ash powder) with sorbents at diverse agitation speeds is mentioned in Table 5. The % MRD clearing improved as the agitation velocity increased from 50 to 100 rpm. As a result, the best agitation rate speed was fixed at 100 rpm. The % MRD removal dropped as the agitation velocity was raised after that. The enduring capability of thin layer sorbent decreased as agitation velocity increased, indicating that the MRD engaged with the sorbent (Potgieter et al., 2021; Giwa et al., 2021). Since the sorbent active regions were saturated with MRD at the best agitation speed, the percentage of MRD clearance fell.

79.5

75.4

Conclusion

85.2

The biosorption potential of *E. hirta*'s leaf powder/bark powder/leaf ash/bark ash towards MRD was explored for the first time. The impact of pH, sorbent dosage, agitation speed of mechanical shaker, temperature, initial MRD quantity and equilibration time on the biosorption potential of *E. hirta*'s leaf powder/bark powder/ leaf ash/bark ash was studied. For all investigated sorbents, maximum percentage MRD clearance was attained at pH unit 4, with a dose quantity of 1.2 gm/l and at ambient temperature of 27 °C. The current analysis concluded that readily accessible *E. hirta*'s might be an effective sorbent for eliminating MRD from aqueous systems.

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Conflict of interest

The authors declare that they have no conflict of interest.

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