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A NOVEL STRATEGY TOWARDS AGRO-WASTE MEDIATED DYE BIOSORPTION FOR WATER TREATMENT

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ABSTRACT

Dyes are used extensively in sectors such as food, drug, cosmetics, textile, ink, toner, press and automotive industries for coloration purposes. Dyes have toxic, mutagenic and carcinogenic effects which pose threat to the environment and aquatic life on being released directly without treatment. However, the available treatment methods are not only costly but also time consuming. In view of the background there is a growing need to develop more cost effective, rapid and environmentally benign methods for treatment of toxic dyes. Biosorption can be used for effective removal of dyes from environment using agricultural wastes. Herein we report the effective removal of industrially important five dyes, namely crystal violet, safranin, methylene blue, brilliant green and bromothymol blue using peels of *Citrus limon*, *Citrus limetta*, *Cucumis sativus*, *Luffa acutangula* and *Solanum tuberosum*. *C. sativus* peel showed maximum biosorption of crystal violet and safranin upto 96.78% at 30 min incubation and 99.78% at 20 min, respectively. *L. acutangula* and *S. tuberosum* exhibited 100% biosorption at 30 min against brilliant green while *S. tuberosum* showed 95.15 % biosorption of methylene blue instantly. *Citrus limon* peel showed 100% biosorption of bromothymol blue in 10 min. Thus, it is evident that the agro-waste can be proved to be most significant for water treatment. Evaluation of optimized parameters will help to develop further a green management technique for environmental remediation by dye removal from water.

KEYWORDS: Agro-waste, *Citrus limon*, *Citrus limetta*, *Cucumis sativus*, *Luffa acutangula*, *Solanum tuberosum*, dye biosorption.

INTRODUCTION

One of the most extensively used triphenylmethane dye is crystal violet (CV), which has broad spectrum applications in human and veterinary medicine, textile industries, paints and printing ink. It is also a potent mutagen and bacteriostatic agent. Similarly, it prevents fungal growth in poultry feed. However, it is recalcitrant dye molecule that persists in environment for a long period which acts as a mitotic poison, potent carcinogen and a potent clastogene promoting tumor growth in fish.[1] Similarly dyes like safranin are hazardous as they act as irritant to skin, eye and toxic to blood, kidneys, nervous system, reproductive system, liver, heart and upper respiratory tract.[2] Methylene blue is similarly considered as one of the potentially harmful dye due to its severe central nervous system toxicity in spite of its use for various conditions, including, methemoglobinemia, vasoplegia and parathyroidectomy.[3] Bromothymol blue and brilliant green are also most widely used commercially available dyes which are potential irritants and are regarded as biohazard substances. Although, there are diverse physico-chemical methods such as adsorption, coagulation and ion-pair extraction reported for the removal of hazardous dyes, but these methods have several limitations towards complete removal of dyes from industrial wastewater and also produce large quantity of sludge containing secondary pollutants.

In view of the background, novel methods using biological materials are regarded as rapid, cost-effective and eco-friendly for the treatment of industrial wastewater polluted with dye. Hence as a part of our growing interest towards exploration of the medicinal plants for novel industrial processes we have studied the potential of peels of various fruits and vegetables for effective removal of dye. Medicinal plants like *Dioscorea bulbifera, Dioscorea oppositifolia, Gnidia glauca, Gloriosa superba, Barleria prionitis, Litchi chinensis,* are rich source of various bioactive principles which show antidiabetic, anticancer, antioxidant, antimicrobial and nanobiotechnological promises.[4-24] However, the peels of the fruits and vegetables are unused waste materials which might have potential for biosorption of environmentally harmful industrial dyes.

Herein we report for the first time the detailed biosorption potential of *Citrus limon*, *Citrus limetta*, *Cucumis sativus*, *Luffa acutangula* and *Solanum tuberosum* peels against five commercially available hazardous dye, namely crystal violet, safranin, methylene blue, brilliant green and bromothymol blue.

MATERIALS AND METHODS

Adsorbent Preparation

Fresh lime (*C. limon*), sweet lime (*C. limetta*), cucumber (*C. sativus*), potato (*S. tuberosum*) and ridge gourd (*L. acutangula*) were collected from farms of Pune, India and thoroughly washed under running tap water for 10 min. The peels were carefully separated and chopped into fine pieces which were dried in hot air oven at 60°C in order to gradually reduce the water content. The dried material was grinded to fine powder using an electric blender.

UV-visible spectroscopy

Five dyes namely, crystal violet, safranin, bromothymol blue, methylene blue and brilliant green were procured from Sigma Aldrich and appropriate weight of each dye was dissolved in distilled water to get 10 µM stock solution. UV-visible spectra was recorded in a range from 300 to 800 nm to evaluate the absorbance maxima (λ_{max}) of each dye. Standard graph was prepared by making serial dilutions of each dye from 1 to 10 µM and by recording absorbance at their corresponding λ_{max} which were used for evaluation of dye concentration in the successive experiments.

Biosorption

In order to initiate the biosorption 1 g of peel from each of lime (*C. limon*), sweet lime (*C. limetta*), cucumber (*C. sativus*), potato (*S. tuberosum*) and ridge gourd (*L. acutangula*) was suspended into 50 mL of 10 µM dye solutions (crystal violet, safranin, brilliant green, bromothymol blue and methylene blue) in separate Erlenmeyer flask. The mixtures were kept on shaker (120 rpm) for 30 minutes. At regular time intervals i.e 0 min, 10 min, 20 min, 30 min an aliquot of 10 ml was withdrawn and centrifuged at 14,000 rpm for 5 min. The supernatant was collected and absorbance was recorded at the corresponding λ_{max} of the respective dye solution. Residual dye in the supernatant was found by extrapolating on the standard graph. Percentage dye biosorption was evaluated by using the following formula.

$$\text{Percentage biosorption} = \frac{\text{Absorbance}_{\text{Control}} - \text{Absorbance}_{\text{Test}}}{\text{Absorbance}_{\text{Control}}} \times 100$$

RESULTS

UV-visible spectroscopy

UV-visible spectra of the test dyes, namely crystal violet, safranin, methylene blue, brilliant green and bromothymol blue recorded at a concentration of 10 µM indicated the absorbance

maxima of the corresponding dyes. Safranin showed an absorbance maxima at 500 nm while brilliant green, bromothymol blue and crystal violet showed an absorbance maxima at 600 nm (Fig. 1). However, methylene blue showed a sharp peak at 650 nm indicating its absorbance maxima.

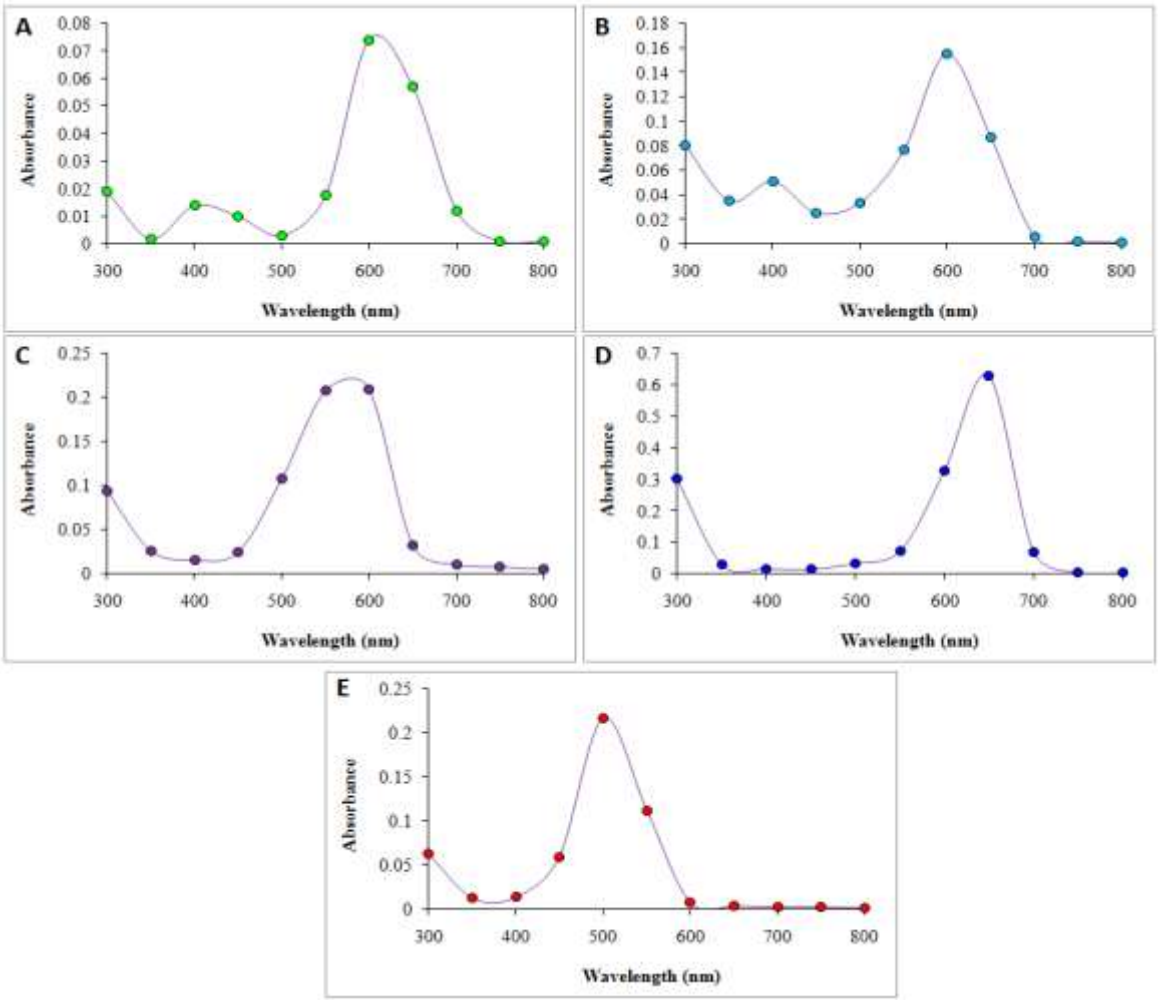

Figure 1: UV-visible spectra of dyes at a concentration of 10 µM. A) Brilliant green; B) Bromothymol blue; C) Crystal violet; D) Methylene blue; E) Safranin.

Standards graphs were prepared by extrapolating the absorbance at λmax for the respective dye at different concentrations ranging from 1µM to 10 µM (Fig. 2). The standard graphs were used to calculate the residual dye in the reaction mixture after biosorption using the peel powders.

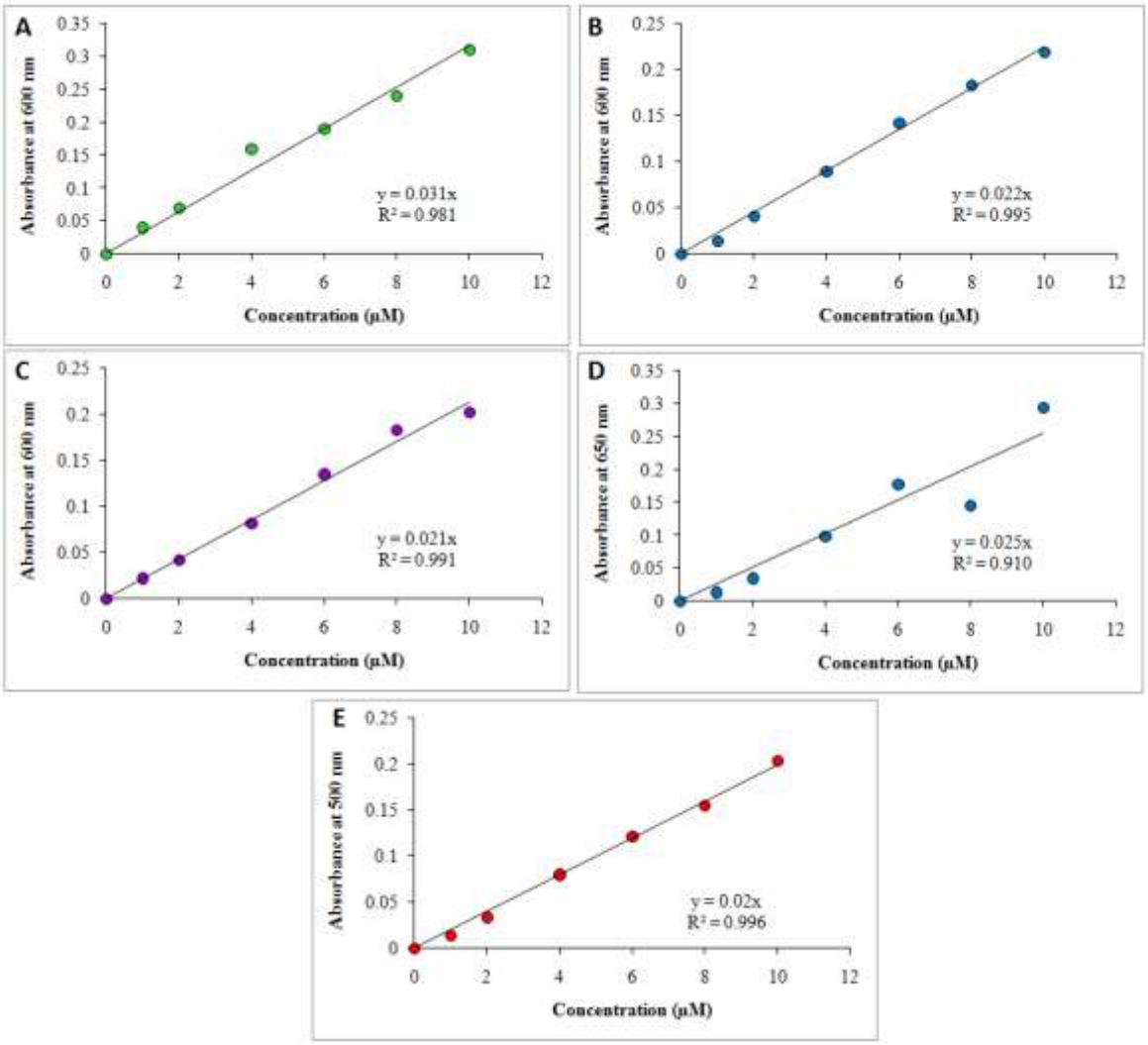

Figure 2: Standard graphs of various dyes recorded at their respective λ_{max}. A) Brilliant green; B) Bromothymol blue; C) Crystal violet; D) Methylene blue; E) Safranin.

Dye biosorption by *C. sativus* peel

Various peel powder showed a varied levels of biosorption of the commercially available dyes. *C. sativus* showed a biosorption percentage as high as 99 % and above with safranin (Fig. 3). Crystal violet was biosorbed upto 79.21 % on exposure till 10 min which gradually increased upto 96.78% with exposure till 30 min. *C. sativus* peel exhibited a maximum biosorption upto 68% against methylene blue. However, a lower biosorption percentage was recorded against bromothymol blue with a maximum value of 26.03%. A very high brilliant green biosorption percentage upto 99.5 % was observed within 20 min of exposure.

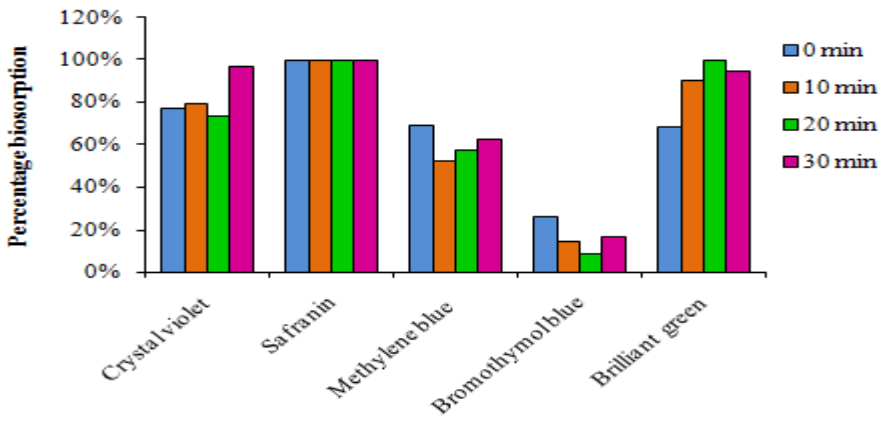

Figure 3: Biosorption of various commercial dyes by *C. sativus* peel.

Dye biosorption by *C. limon* peel

C. limon peel showed an increase in biosorption of crystal violet from 10 mins (85.15%) to 20 mins (90.13%). Biosorption of safranin was found in a range between 87% to 89% (Fig. 4). A lower biosorption percentage was observed against methylene blue which increased upto 31.45% at 30 min. A very high biosorption with bromothymol blue was observed at 10 mins. A similar trend was observed even in case of brilliant green where 90.03% biosorption was observed at 10 min.

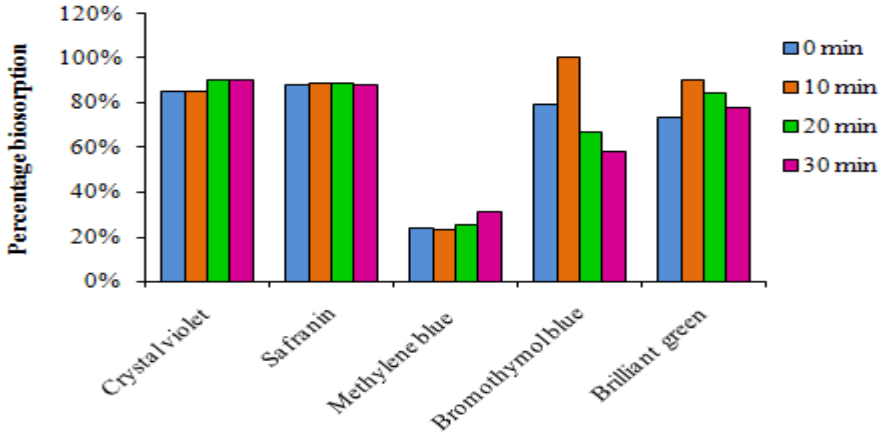

Figure 4: Biosorption of various commercial dyes by *C. limon* peel.

Dye biosorption by *S. tuberosum* peel

S. tuberosum exhibited maximum biosorption against crystal violet and safranin upto 88.89% and 90.33% at 10 min (Fig. 5). Methylene blue was instantly biosorbed with a very high efficiency upto 95.15%. *S. tuberosum* showed comparatively lower biosorption efficiency upto 41.65% against bromothymol blue. Brilliant green could be efficiently biosorbed with gradual increase in time.

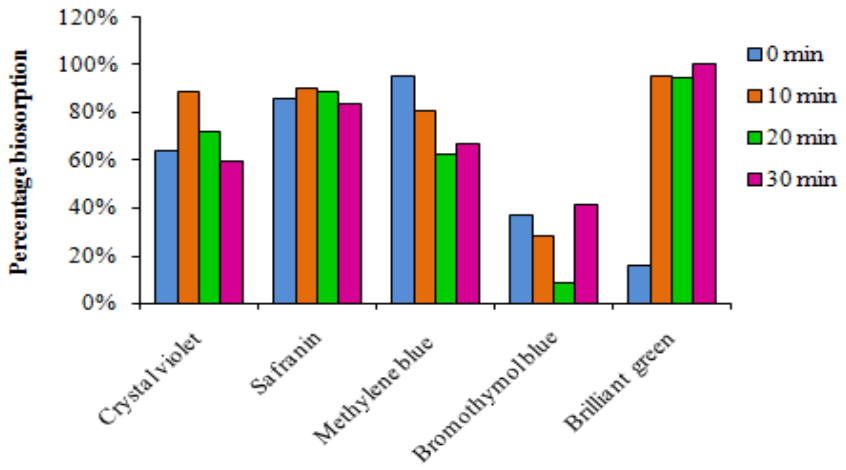

Figure 5: Biosorption of various commercial dyes by *S. tuberosum* peel.

Dye biosorption by *L. acutangula* peel

Biosorption of crystal violet and bromothymol blue between 77-79 % was found to be instant and extremely rapid with *L. acutangula* peel (Fig. 6). At the same time biosorption of safranin and methylene blue was consistent and stable till 30 min. However, biosorption of methylene blue was comparatively lesser than safranin using *L. acutangula* peel. Similarly *L. acutangula* peel was found to be very superior biosorbing agent of brilliant green showing more than 94% at all tested time points.

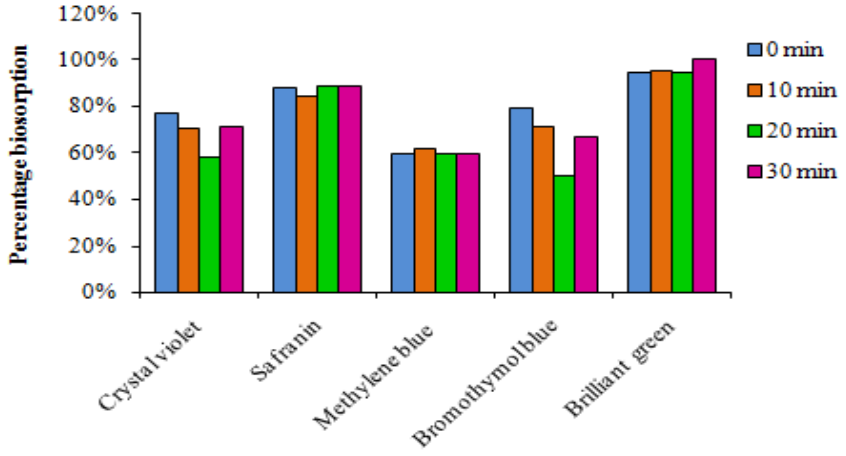

Figure 6. Biosorption of various commercial dyes by *L. acutangula* peel.

Dye biosorption by *C. limetta* peel

C. limetta peel showed efficient biosorption of crystal violet upto 90.13% at 30 min (Fig.7). Biosorption of safranin was found to be fairly consistent in a range between 83 to 86%. However, methylene blue showed a reduced biosorption of 33.06%. *C. limetta* peel exhibited

superior biosorption potential upto 78.61% against bromothymol blue at 10 min. On the other hand brilliant green was instantly biosorbed upto 90.34% by *C. limetta* peel.

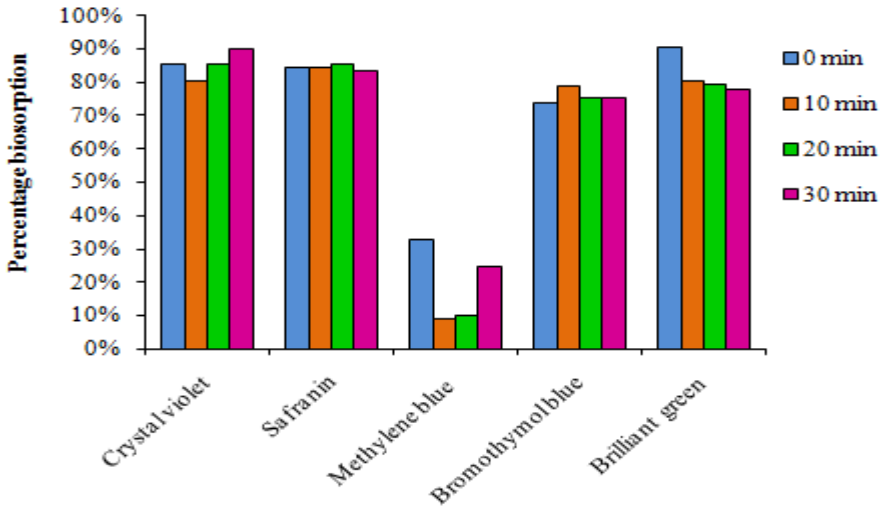

Figure 7: Biosorption of various commercial dyes by *C. limetta* peel.

DISCUSSION

Environmental pollution with hazardous dyes due to urbanization and rapid growth of textile industries has posed a serious threat to human health and ecology. Textile dyes constitute a major source of pollution which on disposal generate different toxic products that might lead to ulceration of skin, and mucous membrane, dermatitis, perforation of nasal septum, severe irritation of respiratory tract and on ingestion may cause vomitting, pain, haemorrhage and sharp diarrhea.[25] Thus various microorganisms like bacteria, fungi, yeasts and algae are exploited for efficient removal of dyes from the effluent. Fungus like *Phanerochaete chrysosporium* are reported to remove azo dyes. Likewise, *Trichoderma harzianum* is reported to remove and degrade various hazardous dyes likes, congo red, acid red, basic blue and bromophenol blue, direct green. Certain algae like *Chlorella pyrenoidosa, Chrorella vulgaris* and *Oscillateria tenius* remove azo dyes by decomposing into simpler aromatic amines. Bacteria like *Pseudomonas aeruginosa, Pseudomonas putida, Bacillus cereus, Bacillus megaterium* are also reported to biosorb and biodegrade various toxic dyes.

However, culturing and microbial biomass generation is economically not viable and labour intensive. Hence, we have studied the agro-wastes like fruit and vegetable peels for efficient removal of the commercially available hazardous dyes. In our study we have observed that dry peel powder of both fruits and vegetables could effectively biosorb crystal violet and

safranin. Among various vegetable peels *C. sativus* peel could remove safranin and brilliant green most effectively. A variation in the biosorption potential was observed among both the peels and dyes. *C. limon* peel showed most superior biosorption of bromothymol blue. Likewise brilliant green was significantly removed using *S. tuberosum, L. acutangula*, *C. limetta* peel. Our observations are in close agreement with the earlier reports where peels of *Punica granatum* L.,(pomegranate), *Ananas comosus* Merr., (pineapple), *Citrullus lanatus* (watermelon), *Allium sativum* (garlic), *Pisum sativum* (green pea) and *Cajanus cajan* (pigeon pea), *Carica papaya* seeds, *Annona squmosa* seed, Banana trunk fibres, Yam leaf fibres, Cassave peel waste, Hazelnut seeds were reported to be superior bioadsorbents.[26-32] Hence this strategy can be considered as one of the most efficient environmentally benign method of bioremediation.

CONCLUSIONS

In this study, we have presented the promises of agro-waste mediated dye biosorption for water treatment which can prove to be a novel strategy towards effluent treatment. Peels of *Citrus limon, Citrus limetta, Cucumis sativus, Luffaa cutangula* and *Solanum tuberosum*. *C. sativus* peel exhibited excellent biosorption specifically against crystal violet and safranin.Similarly, *L. acutangula* and *S. tuberosum* peels exhibited very high biosorption rates against brilliant green while *S. tuberosum* exhibited most superior dye removal with methylene blue most instantly. Likewise *Citrus limon* peel showed complete biosorption of bromothymol blue in 10 minutes. Thus, this report highlights a green-technology for management of dye disposal mediated environmental pollution.

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