Chemical Modification of *Oryza sativa* Linnaeus Husk with Urea for Removal of Brilliant Vital Red and Murexide Dyes from Water by Adsorption in Environmentally Benign Way

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Summary: *Oryza sativa* Linnaeus is an important food item all around the world. Due to its huge consumption, a large amount of rice husk is generated as agrowaste which can be used for water treatment by adsorption. Its adsorption capacity further can be enhanced by chemical medication. In the present study, urea modified rice husk has been used for removing Brilliant Vital Red and Murexide form water in an efficient way. After optimizing operating conditions, isothermal and thermodynamical studies were carried out, which showed that maximum adsorption capacity of urea modified rice husk for removing Brilliant Vital Red and Murexide dyes were 28.93 and 30.74 $mg.g^{-1}$. Adsorbent characterization was carried out by recording its FT-IR spectra.

Keywords: Adsorption, Brilliant Vital Red, Murexide, rice husk, Urea Modification, Isotherms.

Introduction

Waste waters from textile and paper printing industries contain a bulk amount of unemployed dyes and supplementary chemicals together with huge quantity of consumed water [1]. There are various structural diversities in dyes type like cationic, anionic, anthraquinone based and metal complexes [2]. Anionic dyes are commonly known as acidic dyes and widely employed in textile dyeing. Most of the organic dyes have complex chemical structure, due to which they are resilient to breakdown and treat by physio-chemical and biological methodologies [3, 4].

Various types of methods are either used separately or in combination for removing these dyes. In recent years adsorption using various types of agrowaste materials like rice husk, wheat husk, plant leaves, peels of orange, lemon, water melon, banana, peanut etc have been used for removing dyes from water at laboratory scale [5-10]. Use of such materials as adsorbent is cost effective, economical, environmentally benign and easy to handle.

Oryza sativa Linnaeus husk is used in following study. It belongs to plant family Poaceae. Rice husk is a low-value agrowaste. It is already reported as an efficient adsorbent for removing textile dyes such as Malachite Green, Congo red, Methylene Blue, Murexide, Brilliant Vital Red and Acid Yellow 36 in raw form [11-17]. Scientists are trying to improve the natural adsorption capacities of adsorbents by physical and chemical processings like ashing, composites formation, treating with chemicals either in solution form or in solid states etc. In present study, urea modification of rice husk is carried out and then it is employed to remove Murexide and Brilliant Vital Red dyes from water at laboratory scale with better efficiency as already reported [17, 18].

The chemical structure of Brilliant Vital Red and Murexide dyes are given in Figs. 1 and 2 respectively. Other name of Brilliant Vital Red ($C_{34}H_{25}N_6Na_3O_9S_3$) dyes are Ditolyldiazo-3,6-disulfo-β-naphthylamine-β-naphthylamine-6-sulfonic acid sodium salt, Brilliant Congo Red and Direct Red 34. It is used in blood volume determinations, dyeing cotton and paper printing [18, 20-23].

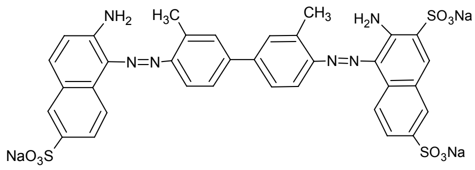

Fig. 1: Brilliant Vital Red dye Structure.

Whereas Murexide ($NH_4C_8H_4N_5O_6$) dye shows color variation from yellow in strongly acidic pH to violet in weakly acidic media and bluish-purple in strongly alkaline media.

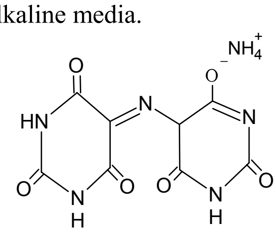

Fig. 2: Murexide.

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It is used as a complexon indicator for calcium determination for water hardness. It is also used for spectrophotometric determinations of various metal ions like calcium, strontium cobalt, nickel, copper, zinc and cadmium [19, 24-26].

Results and Discussion

Surface Characterization of Adsorbent

The FT-IR spectra of simple, non modified rice husk and urea modified rice husk were recorded and vibrational assignments were mentioned in Table-1. It shows that rice husk has different functional groups like amine, carbonyl, hydroxyl etc, whereas in urea modified form hydroxyl groups are missing, but amino and carbonyl groups peaks are strong. Like other lingo-cellulosic compounds, stretching of C–H bond of $-CH_3$ and $–CH_2$ groups was depicted by a single peak at 2889.2 and 2621.8 cm^{-1} [25-28].

Table-1: FT-IR surface characterization of rice husk before and after urea modification.

Vibrational assignments (cm^{-1})	Non modified Rice husk	Urea modified rice husk
N–H stretching	4319, 4248.4, 3881.2	3782.2
OH stretching	3368.5	-
C–H stretching	2889.2	2621.8
C=O, C=C stretching	1632	1675.0
C–H bending	1469.8, 1386.3, 773.7, 727.3	1460, 1365.5, 725
C–O–C stretching	1049.9	1042.5

Optimization of Factors Affecting Adsorption Rate of Dyes

Different factors were studied in order to check its optimized conditions which show more favorable adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes by urea modified rice husk and results are shown in Figs. 3-7.

1. *Adsorbent Dose*

Adsorbent dose variation effect on the adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes by urea modified rice husk is given in Fig. 3. Maximum removal of Murexide (M) and Brilliant Vital Red (B.V.R) dyes occurred when adsorbent dose was 0.8 and 1.2 g respectively. After that, adsorption rate decreased first and then become constant. Increase in adsorption at lower adsorbent does was attributed to the availability of more adsorption sites, which usually decreases at higher adsorbent dose due to the particle interactive behavior like aggregation that ultimately lead to decrease in total surface area of adsorbent [18, 19].

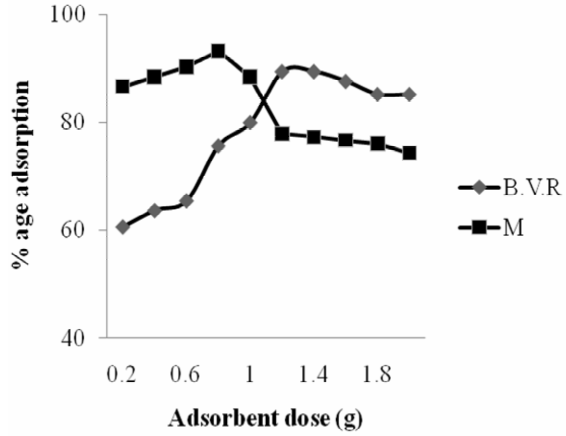


Fig. 3: Adsorbent dose effect on % age adsorption of Brilliant Vital Red and Murexide dyes by urea modified rice husk.

2. *Contact Time Interval*

Contact time interval variation between dyes solutions and urea modified rice husk was studied and graphically represented in Fig. 4.

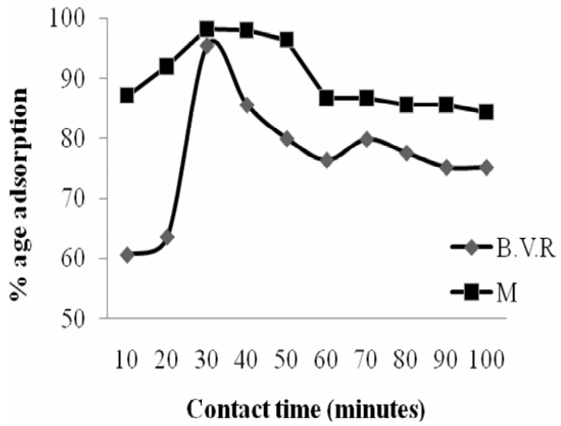


Fig. 4: Contact time effect on Brilliant Vital Red and Murexide dyes adsorption by urea modified rice husk.

It is showing that maximum adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes occurred when contact time interval was 30 minutes in both cases. After that, adsorption rate decreased first and then become constant because of all available sites on urea modified rice husk were covered.

3. *pH of Dye Solution*

The pH of solution affects the existence of ionized and no-ionized species in aqueous media. In acidic conditions, ionized forms of dyes exist more, which helps in removal of dyes by protonated adsorption sites. The results of pH factor effect on adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes by urea modified rice husk are shown in Fig. 5. Maximum removal of Murexide (M) and Brilliant Vital Red (B.V.R) dyes occurred at pH 2. In strongly acidic conditions, urea modified rice husk is more protonated which helps in chemisorptive removal of anionic dyes from water. Strong hydrogen bonding between the oxygen atoms of Murexide (M) and Brilliant Vital Red (B.V.R) dyes and hydroxyl groups of urea modified rice husk contributed in enhanced adsorption efficiency [18].

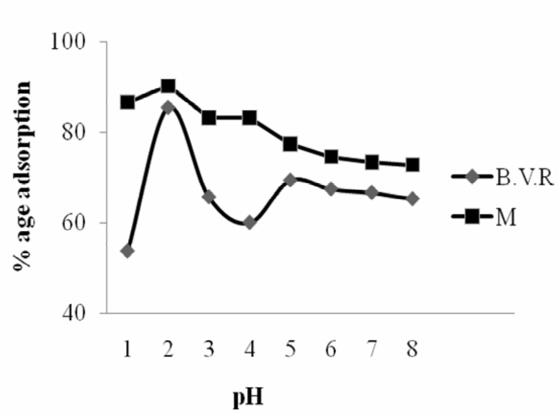


Fig. 5: Effect of pH on %age adsorption of Brilliant Vital Red and Murexide dyes by urea modified rice husk.

4. *Agitation Speed of Dye Solution*

Agitation of dye solution during adsorption enhances its contact with active binding sites of urea modified rice husk. It is clear form Fig. 6. Maximum adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes by urea modified rice husk occurred at 150 rpm. Slower agitation reduces contact between adsorbate and adsorbent and greater speed has negative impact on adsorption process [28].

5. *Temperature*

This factor results are given in Fig. 7. Maximum adsorption of Murexide (M) and Brilliant Vital Red (B.V.R) dyes by urea modified rice husk occurred at 30 and 40 °C respectively.

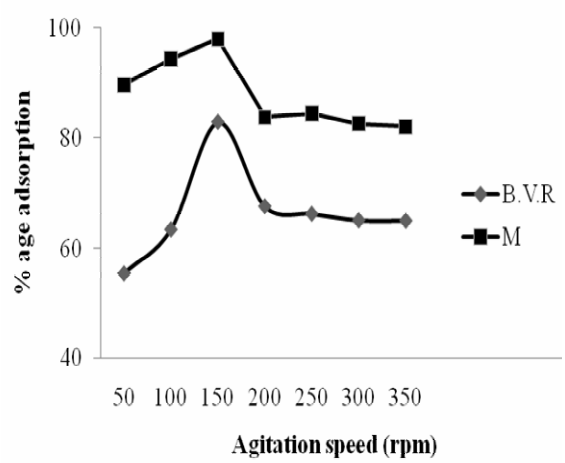


Fig. 6: Effect of stirring speed on %age adsorption of Brilliant Vital Red and Murexide dyes by urea modified rice husk.

At higher and lower temperatures, adsorption decreases. This decrease in adsorption efficiency was attributed to the fact that at high temperature Murexide (M) and Brilliant Vital Red (B.V.R) dyes molecules move with larger speed and less time of interaction was available for adsorbate with urea modified rice husk.

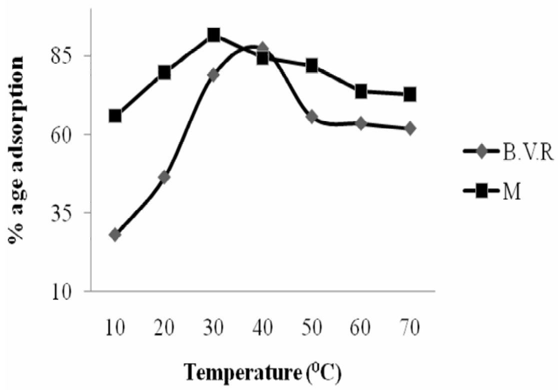


Fig. 7: Effect of temperature on %age adsorption of Brilliant Vital Red and Murexide dyes by urea modified rice husk.

Table-2: Isothermal parameters for adsorption of Brilliant Vital Red and Murexide dyes on urea modified rice husk.

Dyes	Langmuir Isotherm Parameters					Freundlich Isotherm Parameters				
	Slope	Intercept	R^2	q_m (mg.g^{-1})	b (L.g^{-1})	Slope	Intercept	R^2	K_F	n
Murexide	9.987	0.033	0.943	30.74	0.003	0.845	-0.824	0.973	0.15	1.183
Brilliant Vital Red	0.581	0.035	0.985	28.93	0.059	0.430	0.627	0.977	4.23	2.325

6. *Isothermal and Thermodynamic Modeling of Equilibrium Data*

a) *Langmuir Modeling*

Table-2 is showing Langmuir isothermal parameters for adsorption of Murexide and Brilliant Vital Red dyes by urea modified rice husk. The correlation coefficient 'R^2' values in Langmuir model are 0.943 and 0.985 for Murexide and Brilliant Vital Red dyes respectively, showing the applicability of this model on equilibrium data. Its applicability shows that chemisorption is the main mode of adsorptive removal of these dyes with urea modified rice husk. Maximum adsorption capacity 'q_m' for adsorption of Murexide and Brilliant Vital Red dyes by urea modified rice husk were 30.74 and 28.93 $mg.g^{-1}$ respectively. The adsorption mechanism for the removal of these dyes may be supposed to involve the following three steps:

a. diffusion of dyes through the boundary layer,
b. followed by intra-particle diffusion, and
c. adsorption of the dyes on the urea modified rice husk active binding sites [18, 19].

The boundary layer resistance between dyes molecules and adsorbent surface would be altered by the rate of adsorption and increased contact time, which reduced the resistance and results in improved mobility of dyes during adsorption.

b) *Separation Factor 'R_L' and Thermodynamic Parameter 'ΔG^o'*

Second Langmuir parameter 'b' is used for determining separation factor 'R_L' and thermodynamic parameter 'ΔG^o' for adsorption of Murexide and Brilliant Vital Red dyes by urea modified rice husk and given in Table-3. Separation factor value less than one is an indication of favorability of adsorption system. Its value for Murexide and Brilliant Vital Red dyes was 0.869 and 0.253 respectively; means adsorption of these dyes was favorable with urea modified rice husk.

'ΔG^o' explains the thermodynamic feasibility of any reaction. Its value for adsorption of Murexide and Brilliant Vital Red dyes by urea modified rice husk is -14.392 and -7.012 $KJ.mol^{-1}$ correspondingly. These negative values predict the feasibility of this adsorption process on bigger scale. Relatively smaller value for Brilliant Vital Red dye as compared to Murexide is attributed to its complex structure which hinders in its adsorption [17, 29].

Table-3: Separation factor and thermodynamical parameters for adsorptive removal of Brilliant Vital Red and Murexide dyes by urea modified rice husk.

Dyes	Separation factor R_L	Gibbs Free Energy ($KJ.mol^{-1}$)
Murexide	0.869	-14.392
Brilliant Vital Red	0.253	-7.012

c) *Freundlich Modeling*

This isotherm is applicable on those adsorption equilibria where heterogeneous nature of adsorbent and multi-layer physiosorption phenomenon is predominant during removal of pollutant. It is clear from Table-2 that physiosorption is equally important mode of dyes removal along with chemisorptive mode, which is indicated from correlation coefficient 'R^2' values for Freundlich model that is close to unity. Adsorption intensity parameter 'n' values between 1-8 are an indication of strong physiosorption [28-32].

Experimental

Chemical Reagents and Instrumentation

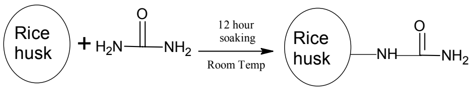
Brilliant Vital Red (Fluka, λ_{max} = 500 nm, Mol. wt = 826.76 $g.mol^{-1}$, color in solid state: Cherry red), Murexide (Fluka, λ_{max} = 520 nm, Mol. wt = 284.19 $g.mol^{-1}$, color in solid state: reddish purple), urea, NaOH, HNO_3, H_2SO_4, CH_3COOH and HCl (Merck) were used. Rice husk was collected from farm-lands of University of Punjab, Lahore, Pakistan. UV/Vis spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD= 3500) was used for measuring dye concentration in standards and working solutions.

Standard Solutions

For making 1000 ppm stock solution of dyes, 1.0 g was taken in 1000 mL measuring flask separately for both dyes and diluted up to the mark with double distilled water. Further solutions of dyes were prepared by successive dilution of stock solutions separately for Murexide and Brilliant Vital Red dyes [18, 19].

Chemical Modification of Adsorbent with Urea

Rice husk was crushed by grinding and soaked in 10 % urea solution for 24 hours. Then it was filtered off and dried in sunlight for one week. After complete drying, it was ground and sieved through 60 mesh for using in adsorption experiments. Processed and chemically modified rice husk was stored in air tight jars till further use. The chemical reaction is graphically presented as in equation 1:



(1)

Powdered untreated rice husk and chemically modified rice husk were analyzed by recording its FT-IR spectra in the range of 800-4000 cm^{-1} FT-IR Spectrometer (Perkin Elmer BX Model) [26].

Adsorption Experiments and Mathematical Modeling of Equilibrium Data

The effect of different operational conditions on the adsorption of Murexide and Brilliant Vital Red dyes by urea modified rice husk was studied in batch mode within following ranges: adsorbent amount (0.2-2.0g), contact time (10-100 min), pH of dye solutions (1-8), agitation speed (50-350 rpm) and temperature (10-70 °C). Dyes solution volume (V) was 50 mL and initial concentration of dyes (C_o) in all experiments was 25 ppm. pH was maintained by 0.01 M HCl and / or NaOH solutions and remaining dye concentration (C_e) in filtrate was determined spectrophotometrically, for calculating % age adsorption.

$$\%\text{age adsorption} = [(C_o - C_e)/C_o] \times 100 \qquad (2)$$

Optimized conditions were employed to higher concentrations of both dyes solutions ranging between 30-90 ppm and the corresponding Langmuir isotherm parameters were determined by regression analysis of the linear plot of '1/q' versus '1/ C_e' using eq. 3 [28, 29]:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \qquad (3)$$

Whereas

$$q = \frac{(C_o - C_e)V}{m} \qquad (4)$$

'q' (mg/g) is the amount of dye adsorbed, 'q_m' ($mg.g^{-1}$) and b ($L.g^{-1}$) are Langmuir isotherm parameters. The value of '*b*' is used for calculating separation factor constant 'R_L' by equation 5 [30]:

$$R_L = \frac{1}{(1 + bC_o)} \qquad (5)$$

The thermodynamic parameter 'ΔG^o' in KJ/mol was determined by eq. 6 using the value of '*b*':

$$\Delta G^o = - RT \ln(K) \qquad (6)$$

Here 'K' is the reciprocal of Langmuir constant 'b'.

The corresponding Freundlich isotherm parameters were determined by regression analysis of the linear plot of 'log q' versus 'log C_e' using eq. 7:

$$\log q = \log K_F + \frac{1}{n} \log C_e \qquad (7)$$

Here 'K_F' and 'n' are Freundlich isotherm parameters [30-32].

Conclusion

It is clear from this study that urea modification of rice husk increased its adsorption capacity to a lager extent, especially for anionic dyes like Murexide and Brilliant Vital red dye. q_{max} values of non modified rice husk for Brilliant Vital Red and Murexide dyes were 10.06 and 15.06 $mg.g^{-1}$ respectively [16, 17], whereas they increased to 28.93 and 30.74 $mg.g^{-1}$ correspondingly for Brilliant Vital Red and Murexide dyes after urea modification of rice husk in this study. So, urea modified rice husk can be employed at larger scale for removal of anionic dyes efficiently.

References

1. B. Noroozi, G.A. Sorial, H. Bahrami and M. Arami, *Dyes and Pigments*, **76**, 784 (2008).
2. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresource Technology,* **77**, 247 (2001).
3. A.R. Gregory, S. Elliot and P. Kluge, *Journal of Applied Toxicology.* **1**, 308 (1991).
4. S.D. Khattri and M.K. Singh, *Water Air and Soil Pollution*, **120**, 283 (2000).
5. A.K. Mittal and S.K. Gupta, *Water Science and Technology*, **34,** 81 (1996).
6. M. Shamsipur and N. Alizadeh, *Talanta*, **39**, 1209 (1992).
7. A.R. Gregory, S. Elliot and P. Kluge, *Journal of Applied Toxicology,* **1**, 308 (1991).
8. F. Perineau, J. Molinier and A. Gaset, *Journal of Chemical Technology and Biotechnology*, **32**, 749 (1982).
9. R. Rehman, A. Abbas, S. Murtaza, T. Mahmud, W. Zaman, M. Salman, U. Shafique, *Journal of the Chemical Society of Pakistan,* **34**, 112 (2012).
10. Y. Guo, S. Yang, W. Fu, J. Qi, R. Li, Z. Wang and H. Xu, *Dyes and Pigments*, **56**, 219 (2003).
11. Y. Guo, H. Zhang, N. Tao, Y. Liu, J. Qi, Z. Wang and H. Xu, *Materials Chemistry and Physics,* **82**, 107 (2003).
12. R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li and L. Zou, *Bioresource Technology*, **99**, 2938 (2008).
13. P. Sharma, R. Kaur, C. Baskar and W. J. Chung, *Desalination*, **259**, 249 (2010).
14. P. K. Malik, *Dyes Pigments*, **56**, 239 (2003).
15. I. A. W. Tan, A. L. Ahmad and B.H. Hameed, *Journal of Hazardous Materials,* **154**, 337 (2008).

16. R. Rehman, J. Anwar, T. Mahmud, M. Salman and U. Shafique, *Journal of the Chemical Society of Pakistan,* **33,** 515 (2011).
17. R. Rehman, J. Anwar, T. Mahmud, M. Salman, U. Shafique and W. Zaman, *Journal of the Chemical Society of Pakistan,* **33**, 598 (2011).
18. M. Karkmaz, E. Puzenat, C. Guillard and J. M. Herrmann, *Applied Catalysis* B*: Environmental*, **51,** 183 (2004).
19. E. Brillas, B. Boye, I. Sires, J. A. Garrido, R. M. Rodríguez, C. Arias, P. L. Cabot, C. Comninellis*, Electrochimica Acta,* **49**, 4487 (2004).
20. G. Zhang, F. Yang, M. Gao, X. Fang and L. Liu, *Electrochimica Acta,* **53,** 5155 (2008).
21. G. L. Baughman, *Environmental Toxicology and Chemistry,* **7**, 183 (1998).
22. N. M. Winslow, *Journal of the American Chemical Society,* **61**, 2089 (1939).
23. E. S. Reynolds and R. E. Linde*, Analytical Biochemistry,* **5**, 246 (1963).
24. H. Gordon and G. Norwitz*, Talanta*, **19**, 1 (1972).
25. D. S. Russell, J. H. Campbell and S. S. Bermaban, *Analytica Chimica Acta*, **25**, 81 (1961).
26. M. Shamsipur and N. Alizadeh, *Talanta*, **39**, 1209 (1992).
27. U. Farooq, M. A. Khan, M. Athar, M. Sakina and M. Ahmad, *Clean–Soil, Air, Water*, **38**, 49 (2010).
28. R. Rehman, J. Anwar and T. Mahmud, *Journal of the Chemical Society of Pakistan,* **34**, 460 (2012).
29. F. Kanwal, R. Rehman, T. Mahmud, J. Anwar and R. Ilyas, *Journal of the Chilean Chemical Society,* **57**, 1058 (2012).
30. U. Shafique, A. Ijaz, M. Salman, W. Zaman, N. Jamil, R. Rehman and A. Javaid, *Journal of Taiwan Institute of Chemical Engineers,* **43**, 256 (2012).
31. R. Rehman, J. Anwar, T. Mahmud, M. Salman, *Journal of the Chemical Society of Pakistan,* **34**, 136 (2012).
32. F. Kanwal, R. Rehman, J. Anwar and T. Mahmud, *Electronic Journal of Environmental, Agricultural and Food Chemistry,* **10**, 2972 (2011).