UTILIZATION OF RICINUS COMMUNIS STEM POWDER FOR SORPTIVE ERADICATION OF METHYLENE BLUE DYE FROM AQUEOUS MEDIA IN ECO-FRIENDLY WAY

*Rabia Rehman, Tariq Mahmud**
Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan
** Corresponding author*
Tel: +92-42-99230463, Ext: 831, Fax: +92-42-99230998, E-mail: tariqm06@yahoo.co.uk

ABSTRACT

Removal of textile dyes from waste-water streams by adsorption methodology is getting importance nowadays. Surge for replacement of activated charcoal with agro-waste materials from native sources is the main aim of this study. Here adsorption capacity of Ricinus communis stem powder had been investigated for removal of Methylene Blue dye. For comparison, Ricinus communis stem powder was treated with formalin to enhance its adsorption capacity. Isothermal and thermodynamic studies were carried out after optimizing adsorption conditions. The results indicated that Ricinus communis stem powder had maximum adsorption capacity of 11.59 mg/g, which is improved after formalin treatment, i.e.19.45 mg/g. Thermodynamic and separation factor values supported the feasibility of this process. S.E.M studies indicated the porous structural aspects of Ricinus communis stem powder, suitable for removing Methylene Blue dye.

Keywords: Ricinus communis stem powder, Methylene Blue dye, adsorption, water treatment.

1. INTRODUCTION

The treatment of waste water is carried out in various ways, in order to remove dyes, pigments, heavy metals, organic pollutants and other biological impurities. Filtration, coagulation, ion exchange, ozonation, photo-catalytic degradation and adsorption on charcoal, are some famous methodologies. But the main problems associated with such techniques are their cost, management and sludge disposal etc. (Rafatullah, et al., 2010). Biosorption of pollutants on some agro-waste material is getting importance as an alternative way of water treatment, because of its low cost, user friendly nature and ease in handling. So, various types of agro-waste materials are investigated in all over the world for removing dyes and other pollutants from water. In this study, *Ricinus communis* stem powder was used to remove Methylene Blue dye from water by adsorption. Other reported adsorbents for this dye are: rice husk (Adam, et al., 2013), globe artichoke leaves (Benadjemia, et al., 2011), Neem leaf powder (Bhattacharyya and Sharma, 2005), wheat shells (Bulut and Aydın, 2006), *Posidonia oceanica* dead leaves (Cavas, et al., 2011), cotton stalk (Deng, et al., 2011), hazelnut shell (Doğan, et al., 2009), swede rape straw (Feng, et al., 2012), oil palm fiber (Foo and Hameed, 2011), spent coffee grounds (Franca, et al., 2009), Indian rosewood sawdust (Garg, et al., 2004), cedar saw dust (Hamdaoui, 2006), garlic peels (Hameed and Ahmad, 2009), rattan saw dust (Hameed, et al., 2007), lotus leaf (Han, et al., 2011), coir pith carbon (Kavitha and Namasivayam, 2007), rejected tea (Nasuha and Hameed, 2011), jute fibers (Senthilkumaar, et al., 2005), peanut husk (Song, et al., 2011), sugar beet pulp (Vargas, et al., 2011) and pineapple leaf powder (Vučurović, et al., 2012).

There are different varieties of synthetic dyes like acidic, basic, disperse, azo, diazo, anthraquinone based and metal complexes which are being used in textile industries [10]. Methylene Blue (M.B, Fig. 1) is a classical, basic dye, originally synthesized by Heinrich Caro in 1876, used for dying hair, leather and cellulosic fibers, redox indicator, ISO test pollutant in semiconductor photo-catalysis, photo-sensitizer for singlet oxygen generation, stain for fixed and living tissues, diagnostic agent in renal function tests, antidote to cyanide and nitrate poisoning and as a treatment for malaria (Mills, et al., 2011, Ponnusami, et al., 2010)

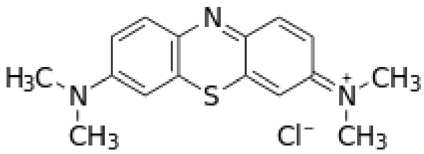

Fig 1. Structure of Methylene Blue.

Ricinus communis (Common name: castor oil plant, family: Euphorbiaceae) is widespread throughout tropical regions. Extract of Ricinus communis has exhibited acaricidal and insecticidal activities. It is used in medicines, cosmetics and biodiesel production. Its stem is hollow, fibrous and mucilaginous with spiky texture. That's why; it is not employed in fuel or fodder. Ricinus communis stem was used as a biosorbent for the removal of Methylene Blue dye in this study. Previous studies have been conducted to remove the heavy metal ions and malachite green dye using its leaves and epicarps which showed its ability to use as adsorbent. Its fruit is mostly used as food and it has also been investigated as an anti-diabetic medicinal plant (Martins, et al., 2013, Niu, et al., 2007, Santhi, et al., 2010).

2. MATERIALS AND METHODS

2.1 Reagents and Instrumentation Used

Methylene blue (M.B) (CI: 52,015; chemical formula: $C_{16}H_{18}ClN_3S$; synonym: Basic Blue-9; molecular weight: 319.86; maximum wavelength: 662 nm) supplied by Merck, was not purified prior to use. HCl, NaOH and formalin were purchased from Merck and Fluka. *Ricinus communis* stems were collected from nearby area of home institute, washed, dried and crushed into fine powder.

2.2 Chemical Treatment of Biosorbent

5.0 g of *Ricinus communis* stem powder was treated with 50 mL of formalin and employed for adsorption of dye after drying at 80 ^oC for 6 hours.

2.3 Adsorption Experiments

All the operational conditions were optimized as described already (Rehman et al., 2012). The % age adsorption of dye at any instant of time was calculated using Eq.1:

$$\%\,\text{age adsorption of dye} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Here C_o and C_e are the initial and final concentrations of dye before and after adsorption in $mg.L^{-1}$.

3. RESULTS AND DISCUSSION

3.1 Surface Characterization

Surface characterization of Ricinus communis stem powder was carried out by Scanning Electron Microscopy (SEM). The results are presented in Fig. 2, which clearly indicated the porous nature of the adsorbent that can adsorb dye from water.

3.2 Effect of Adsorbent Dose:

From Fig. 3, it was indicated that maximum adsorption (94%) occurred with 0.4 g adsorbent dose. After that, due to coagulation of adsorbent particle in solution, further adsorption rate decreased.

4. EFFECT OF CONTACT TIME

Fig. 4 has shown that maximum adsorption 76% occurred at a contact time of 65 minutes. Initially more surface was available for adsorption, but with the passage of time, all adsorption sites were occupied, which resulted in decreased adsorption rate.

5. EFFECT OF PH:

As Methylene Blue is a cationic dye, so it adsorbed more in acidic conditions, due to more ionization. Ionized portion chemisorbed more on Ricinus communis stem powder. So, it is obvious from results that maximum adsorption 86 % occurred at pH 4 as shown in Fig. 5.

6. EFFECT OF AGITATION RATE

Adsorption efficiency was improved by increasing agitation speed, but after a certain optimized condition, it decreased because all binding sites had been utilized and no binding sites were available for further adsorption. Maximum adsorption of Methylene Blue with Ricinus communis stem powder was 73%, which occurred at 100rpm, Fig. 6.

7. EFFECT OF TEMPERATURE

Adsorption equilibrium is a thermo-dependent process. This effect may be due to the fact that at higher temperatures, a decrease in the movement of the solute occurs which results decrease in adsorption. Maximum adsorption of Methylene Blue with Ricinus communis stem powder was 73%, which occurred at 40 ^{o}C, Fig. 7.

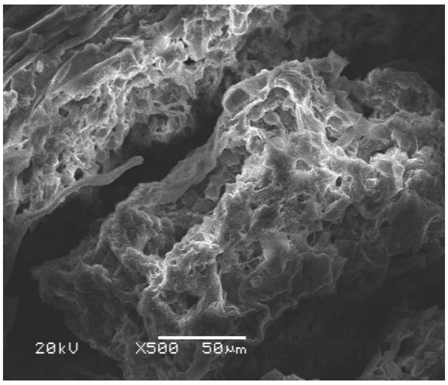

Fig 2. SEM image of *Ricinus communis* stem powder.

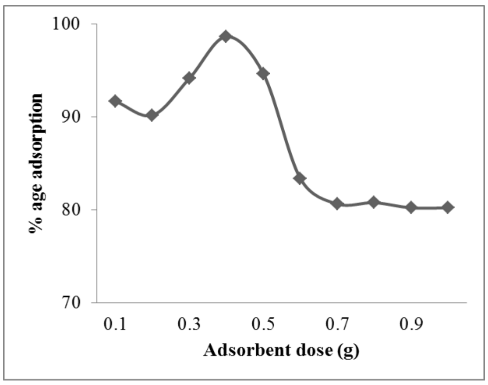

Fig 3. Graph showin effect of adsorbent dosage on Methylene Blue dye adsorption by *Ricinus communis* stem powder.

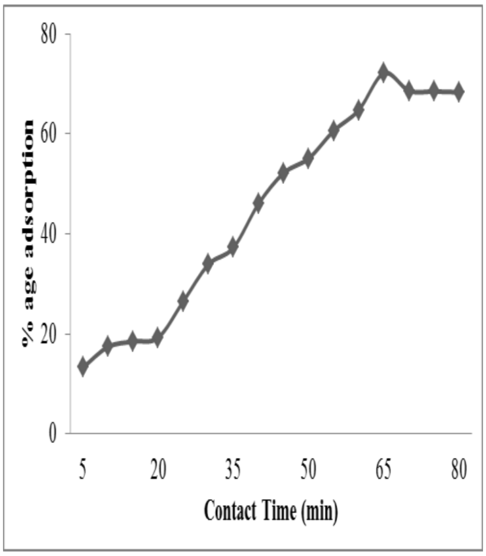

Fig 4. Graphs showing effect of Contact Time on Methylene Blue dye adsorption by Ricinus communis stem powder.

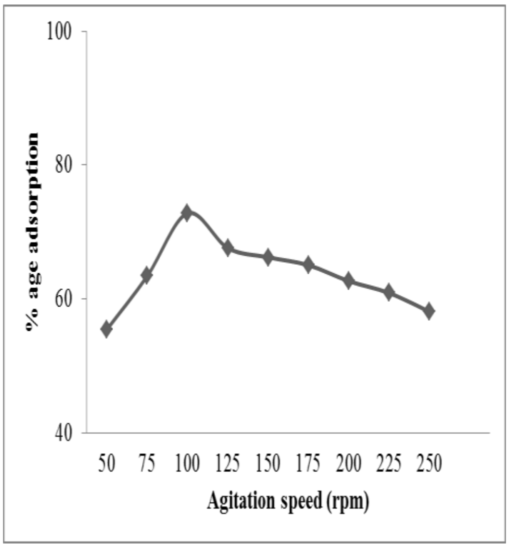

Fig 6. Graph showing effect of agitation speed on Methylene Blue dye adsorption by Ricinus communis stem powder.

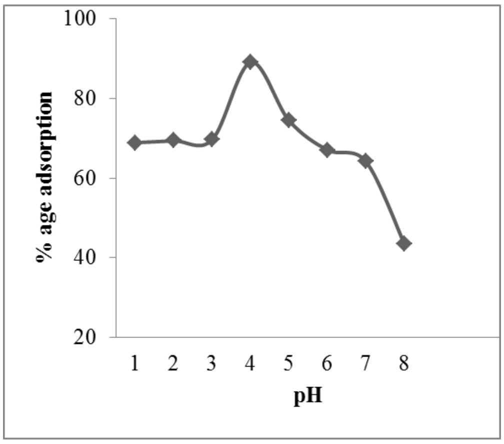

Fig 5. Graph showing effect of pH on Methylene Blue dye adsorption by Ricinus communis stem powder.

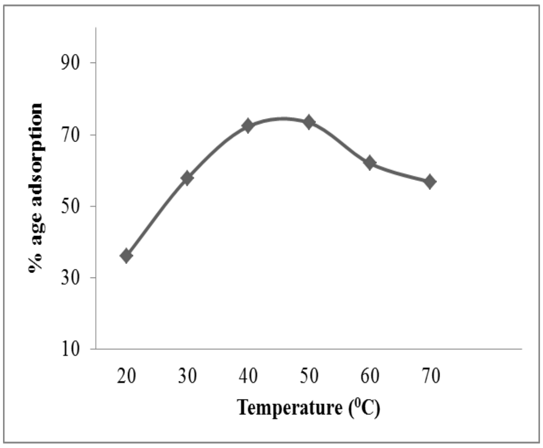

Fig 7. Graph showing effect of temperature on Methylene Blue dye adsorption by Ricinus communis stem powder.

8. ISOTHERMAL AND THERMODYNAMICAL INVESTIGATIONS

Optimized adsorption conditions were applied to remove Methylene Blue dye from water using untreated (U.T.B) and formalin treated (F.T.B) Ricinus communis stem powder and equilibrium data was analyzed by Langmuir model, i.e.:

$$\frac{1}{q} = \frac{1}{bq_m C_e} + \frac{1}{q_m} \tag{2}$$

Where the term *'q'* (mg.g^{-1}) is the amount of dye adsorbed, 'C_e'(ppm) is the remaining dye concentration, 'q_m' (mg g^{-1}) and *b* (L.g^{-1}) are Langmuir constants. Langmuir Separation factor 'R_L' was calculated with Eq. 3:

$$R_L = \frac{1}{(1_o + bC_o)} \tag{3}$$

For calculating 'ΔG^o' Eq. 4 was used:

$$\Delta G^o = -RT \ln K \tag{4}$$

Here 'ΔG^o' is in KJ.mol^{-1}, 'R' is the universal gas constant, *'T'* is the absolute temperature in Kelvin and 'K' is the reciprocal of Langmuir constant '*b*' (Rehman et al., 2012).

Table 1: Langmuir isothermal parameters for Methylene Blue dye sorptive removal by *Ricinus communis* stem powder.

Adsorbent	***Langmuir Isotherm Parameters***					**R_L**	**ΔG^0 ($KJmol^{-1}$)**
	Slope	**Intercept**	**R^2**	**q_{max} (mg.g^{-1})**	**b (L.g^{-1})**		
U.T.B	2.096	0.086	0.982	11.59	0.041	0.328	-7.91
F.T.B	0.545	0.051	0.91	19.45	0.094	0.175	-5.85

Table 2: Comparison of removing capacity of previously reported adsorbents for Methylene Blue dye with present study.

Adsorbent	**q_m (mg.g^{-1})**
Rice husk	4.41
Peanut husk	72.13
Garlic peels	8.62
Banana peels	20.8
Neem leaves	8.76
Orange peels	18.6
Madhuca longifolia leaves	3.66
Fly ash	13.42
Wheat shells	16.56
Eugenia jambolana seeds (J.S)	4.902
Citrullus lanatus peels (W.M.P)	35.714

Correlation coefficient (R^2) values indicated that this model is applicable on this system. It means monolayer chemisorption occurred more during dye removal by the adsorbent. Maximum adsorption intensity 'q_m' values indicated that formaldehyde treatment increased the adsorption capacity of Ricinus communis stem. Comparison of adsorption capacity with other reported adsorbents, which was mentioned in introduction and Table 2, indicated that Ricinus communis stem has a potential to be used for adsorption of Methylene Blue. The values of 'b' clearly pointed out that increase in the adsorption would not occur with increasing temperature because adsorption is generally an exothermic process. Separation factor values are lower than unity in both cases, showing that adsorption of Methylene Blue dye was favorable with Ricinus communis stem. The feasibility of use of Ricinus communis stem powder for adsorption was also indicated by ΔG^o values, which are negative, i.e.: -7.91 and -5.85 for U.T.B and F.T.B.

9. CONCLUSION

From this study, it can be safely concluded that *Ricinus communis* stem powder is a very effective biosorbent for removal of cationic dyes from waste water. Its adsorption capacity can be almost doubled by chemical modification with formalin for removing Methylene Blue dyes especially.

10. REFERENCES

[1]. Adam, F., Muniandy, L., and Thankappan, R. (2013) Ceria and titania incorporated silica based catalyst prepared from rice husk: Adsorption and photocatalytic studies of methylene blue. J. Colloid Int. Sci., 406(0), pp. 209-216. http://dx.doi.org/10.1016/j.jcis.2013.05.066.

[2]. Benadjemia, M., Millière, L., Reinert, L., Benderdouche, N., and Duclaux, L. (2011) Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves. Fuel Process.Tech., 92(6), pp. 1203-1212. http://dx.doi.org/10.1016/j.fuproc.2011.01.014.

[3]. Bhattacharyya, K.G., and Sharma, A. (2005) Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. Dyes Pigments, 65(1), pp. 51-59. http://dx.doi.org/10.1016/j.dyepig.2004.06.016.

[4]. Bulut, Y., and Aydın, H. (2006) A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. Desalination, 194(1–3), pp. 259-267. http://dx.doi.org/10.1016/j.desal.2005.10.032.

[5]. Cavas, L., Karabay, Z., Alyuruk, H., Doğan, H., and Demir, G.K. (2011) Thomas and artificial neural network models for the fixed-bed adsorption of methylene blue by a beach waste Posidonia oceanica (L.) dead leaves. Chem. Eng. J., 171(2), pp. 557-562. http://dx.doi.org/10.1016/j.cej.2011.04.030.

[6]. Deng, H., Lu, J., Li, G., Zhang, G., and Wang, X. (2011) Adsorption of methylene blue on adsorbent materials produced from cotton stalk. Chem. Eng. J., 172(1), pp. 326-334. http://dx.doi.org/10.1016/j.cej.2011.06.013.

[7]. Doğan, M., Abak, H., and Alkan, M. (2009) Adsorption of methylene blue onto hazelnut shell: Kinetics, mechanism and activation parameters. J. Hazard. Mater., 164(1), pp. 172-181. http://dx.doi.org/10.1016/j.jhazmat.2008.07.155.

[8]. Feng, Y., Zhou, H., Liu, G., Qiao, J., Wang, J., Lu, H., Yang, L., and Wu, Y. (2012) Methylene blue adsorption onto swede rape straw (*Brassica napus* L.) modified by tartaric acid: Equilibrium, kinetic and adsorption mechanisms. Bioresource Tech., 125(0), pp. 138-144. http://dx.doi.org/10.1016/j.biortech.2012.08.128.

[9]. Foo, K.Y., and Hameed, B.H. (2011) Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption. Chem. Eng. J., 166(2), pp. 792-795. http://dx.doi.org/10.1016/j.cej.2010.11.019.

[10]. Franca, A.S., Oliveira, L.S., and Ferreira, M.E. (2009) Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. Desalination, 249(1), pp. 267-272. http://dx.doi.org/10.1016/j.desal.2008.11.017.

[11]. Garg, V.K., Amita, M., Kumar, R., and Gupta, R. (2004) Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes Pigments, 63(3), pp. 243-250. http://dx.doi.org/10.1016/j.dyepig.2004.03.005.

[12]. Hamdaoui, O. (2006) Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. J. Hazard. Mater., 135(1–3), pp. 264-273. http://dx.doi.org/10.1016/j.jhazmat.2005.11.062.

[13]. Hameed, B.H., and Ahmad, A.A. (2009) Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. J. Hazard. Mater., 164(2–3), pp. 870-875. http://dx.doi.org/10.1016/j.jhazmat.2008.08.084.

[14]. Hameed, B.H., Ahmad, A.L., and Latiff, K.N.A. (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigments,75(1), pp. 143-149. http://dx.doi.org/10.1016/j.dyepig.2006.05.039.

[15]. Han, X., Wang, W., and Ma, X. (2011) Adsorption characteristics of methylene blue onto low cost biomass material lotus leaf. Chem. Eng. J.,171(1), pp. 1-8. http://dx.doi.org/10.1016/j.cej.2011.02.067.

[16]. Kavitha, D., and Namasivayam, C. (2007) Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. Bioresource Tech., 98(1), pp. 14-21. http://dx.doi.org/10.1016/j.biortech.2005.12.008.

[17]. Martins, A.E., Pereira, M.S., Jorgetto, A.O., Martines, M.A.U., Silva, R.I.V., Saeki, M.J., and Castro, G.R. (2013) The reactive surface of Castor leaf [*Ricinus communis* L.] powder as a green adsorbent for the removal of heavy metals from natural river water. Appl. Surf.Sci., 276(0), pp. 24-30. http://dx.doi.org/10.1016/j.apsusc.2013.02.096.

[18]. Mills, A., Hazafy, D., Parkinson, J., Tuttle, T., and Hutchings, M.G. (2011) Effect of alkali on methylene blue (C.I. Basic Blue 9) and other thiazine dyes. Dyes Pigments, 88(2), pp. 149-155. http://dx.doi.org/10.1016/j.dyepig.2010.05.015.

[19]. Nasuha, N., and Hameed, B.H. (2011) Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. Chem. Eng. J., 166(2), pp. 783-786. http://dx.doi.org/10.1016/j.cej.2010.11.012.

[20]. Niu, Z.-x., Sun, L.-n., Sun, T.-h., Li, Y.-s., and Wang, H. (2007) Evaluation of phytoextracting cadmium and lead by sunflower, ricinus, alfalfa and mustard in hydroponic culture. J. Env. Sci., 19(8), pp. 961-967. http://dx.doi.org/10.1016/S1001-0742(07)60158-2.

[21]. Ponnusami, V., Rajan, K.S., and Srivastava, S.N. (2010) Application of film-pore diffusion model for methylene blue adsorption onto plant leaf powders. Chem. Eng. J., 163(3), pp. 236-242. http://dx.doi.org/10.1016/j.cej.2010.07.052.

[22]. Rafatullah, M., Sulaiman, O., Hashim, R., and Ahmad, A. (2010) Adsorption of methylene blue on low-cost adsorbents: A review. J. Hazard. Mater., 177(1–3), pp. 70-80. http://dx.doi.org/10.1016/j.jhazmat.2009.12.047.

[23]. Rehman, R., Anwar, J., and Mahmud, T., (2012) Thermodynamical and isothermal modeling of Methylene Blue dye batch biosorption on formalin modified *Madhuca longifolia* leaf powder, J. Chem. Soc. Pak., 34 (2), pp. 460-467.

[24]. Santhi, T., Manonmani, S., and Smitha, T. (2010) Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of *Ricinus communis* by adsorption. J. Hazard. Mater., 179(1–3), pp. 178-186. http://dx.doi.org/10.1016/j.jhazmat.2010.02.076.

[25]. Senthilkumaar, S., Varadarajan, P.R., Porkodi, K., and Subbhuraam, C.V. (2005) Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. J. Colloid Interface Sci, 284(1), pp. 78-82. http://dx.doi.org/10.1016/j.jcis.2004.09.027.

[26]. Song, J., Zou, W., Bian, Y., Su, F., and Han, R. (2011) Adsorption characteristics of methylene blue by peanut husk in batch and column modes. Desalination, 265(1–3), pp. 119-125. http://dx.doi.org/10.1016/j.desal.2010.07.041.

[27]. Vargas, A.M.M., Cazetta, A.L., Kunita, M.H., Silva, T.L., and Almeida, V.C. (2011) Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): Study of adsorption isotherms and kinetic models. Chem. Eng. J., 168(2), pp. 722-730. http://dx.doi.org/10.1016/j.cej.2011.01.067.

[28]. Vučurović, V.M., Razmovski, R.N., and Tekić, M.N. (2012) Methylene blue (cationic dye) adsorption onto sugar beet pulp: Equilibrium isotherm and kinetic studies. J. Taiwan Inst. Chem. Eng., 43(1), pp. 108-111. http://dx.doi.org/10.1016/j.jtice.2011.06.008.