



Short communication

Pseudo-kinetics of batch extraction of *Crotalaria juncea* (Sunn hemp) seed oil using 2-propanol



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ABSTRACT

Crotalaria juncea (Sunn hemp) is one of the popular fiber crops of India. Its seeds contain appreciable amount of bio-oil which has promising fuel characteristics. Batch kinetics of extraction of *C. juncea* oil has been carried out and some pseudo-kinetic models (*two-site kinetic desorption model* (TSKDM), *one-site kinetic desorption model* (OSKDM) and second order pseudo-kinetics) are used to validate the experimental outcome. It is found that pseudo-second order kinetics fits more suitably in this case of oil extraction which approves a two stage leaching process, starting with an intense dissolution and scrubbing of maximum oil at the beginning followed by a much slower diffusion stage to remove the residual oil.

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1. Introduction

Crotalaria juncea (Sunn hemp) is one of the early and distinctly named fiber crops of India. Sunn hemp is grown in almost all the states of India either as a fiber crop, green manure or fodder crop. The states of Bihar, Madhya Pradesh, Maharashtra, Rajasthan, Orissa and Uttar Pradesh grow this crop mainly for fiber (Chee and Chen, 1992). Not much work has been actually carried out in the recent past on extraction and characterization of *Crotalaria* oil from its seeds, even though Sunn hemp seeds contain more than 12% oil (Javed et al., 1999; Chaudhury et al., 1978) and it is already reported that it has promising fuel value and this bio-fuel may be economically competitive with the standard diesel fuel (Dutta et al., 2014).

Solid-liquid extraction i.e. leaching is a common and efficient technique for extracting oil from seeds. Leaching involves transfer of soluble fraction (solute i.e. oil) from solids to the solvent phase. The solute diffuses from solid into the surrounding solvent. Generally, solid liquid extraction is dependent on the chemical nature of the solvent and oil, contact time between solvent and seeds, temperature of the process, particle size of the solid, voidage of the packing and the ratio of solvent to the solid. Optimization of all the process parameters for extraction of Sunn hemp oil is already done and the result indicates that 2-propanol is the most suitable

solvent for extraction of Sunn hemp oil from its seeds (Dutta et al., 2014). Batch kinetic study is as important as an equilibrium analysis and the same is essential to understand the mechanism of interaction between solid matrix and solvent in leaching. Driving force for mass transfer (as the oil from seeds get leached out into the solvent) can be visualized as just the reverse of a solute getting adsorbed into a porous media from the adsorbate. Therefore, the pseudo-kinetics of leaching seems to be quite similar to those of an adsorption-desorption process (So and Macdonald, 1986; Wiese and Snyder, 1987; Meziane et al., 2006; Meziane and Kadi, 2008; Rakotondramasy et al., 2007). A solid liquid extraction process is found to be most appropriately fitted by a second order model for leaching (Ho et al., 2005) and adsorption (Reddad et al., 2002; Kim et al., 2005). It takes place in two subsequent stages: firstly, major part of the solute gets extracted quite fast because the dissolution is caused by highest driving force in between the fresh solvent and seed (full of oil); next, external diffusion takes place, whereby the remaining solute goes into the solution, where the extraction process is decelerated as the driving forces weaken.

In this study, considering and expecting the above mentioned mechanism of extraction of oil from seeds, some kinetic models are investigated for the development of kinetics of extraction of *C. juncea* oil using 2-propanol as the solvent.

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2. Experimental details

2.1. Materials and methods

The ground seeds (weight: 10 gm.; size fraction: $-18/+36$) (Dutta et al., 2014) and 100 ml of 2-propanol with a seed to solvent ratio (w/w): 0.1272 (Dutta et al., 2014) are added into a three-necked flask, connected with a condenser. The flask was placed in an isothermal water bath and the temperature was maintained at the boiling point of 2-propanol. No stirring is applied. At the end of a predetermined extraction time, based on the optimum extraction time as required in a Soxhlet apparatus (Dutta et al., 2014), samples of oil-solvent mixtures along with solid were withdrawn after certain intervals of time to measure the time dependent oil yield. In order to measure the amount of extracted oil at a particular time, the oil-solvent mixture is distilled further by simple batch distillation followed by separation of the oil using a rotary evaporator (Make: BUCHI; Model: Rotavapor R-3). In other words, by measuring the dried seed weight after each run and comparing it with the weight of seed previously taken, oil yield can be estimated. The percentage yield is calculated on the basis of the following equation with W_1 being the amount of seed taken in gm, W_{t2} being the amount of oil extracted in gm at time t and W_{t3} being the dried seed weight after extraction time t :

$$\% \text{oil yield} = \left(\frac{W_{t2}}{W_1} \times 100 \right) = \frac{(W_{t3} - W_1)}{W_1} \times 100 \quad (1)$$

The whole experiment is repeated a number of times in order to collect time dependent data and each run is carried out in duplicate. Performance of these models is statistically estimated using a mean relative percent deviation (MRPD) and coefficient of determination (R^2), which are computed using following expressions, respectively,

$$\text{MRPD} = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{p,i} - q_{a,i}}{q_{a,i}} \right| \quad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (q_{p,i} - q_{a,i})^2}{\sum_{i=1}^n (q_{p,i} - q_m)^2} \quad (3)$$

Where, $q_{p,i}$ and $q_{a,i}$ are the predicted and observed values of oil yield, q_m is the mean value of oil yield and n is the number of observations.

2.2. Theory:Pseudo-kinetic models

The rate of leaching should be proportional to a driving force, which is assumed to be the difference between C^* and C_t where C^* ($\text{gm} \times \text{L}^{-1}$) and C_t ($\text{gm} \times \text{L}^{-1}$) are the concentrations of oil in solvent phase at equilibrium and at any time t respectively. Similarly, solute concentration in the solid matrix can be monitored in terms of q_∞ and q where q is the mass of analyte removed by the extraction solvent after time t ($\text{mg} \times \text{gm}^{-1} \times \text{dry sample}$) and q_∞ is the initial mass of analyte in the matrix ($\text{mg} \times \text{gm}^{-1} \text{dry sample}$). The pseudo-chemical order of extraction and rate constant must be determined experimentally. Several models describing the rate of extraction are studied and compared.

2.3. First-order pseudo kinetics of leaching of oil

The overall mechanism of oil extraction from *C. juncea* seeds probably consists of two simultaneous processes: predominant dissolution of oil near the surface of the seed particles, known as washing (bulk) and diffusion of oil (molecular) from the porous seed particles into the bulk of the solution. Therefore, Washing and

diffusion steps are treated collectively to indicate the oil yield with time.

For both washing and diffusion processes, the overall rate of mass transfer, as the oil gets leached from seed to the bulk liquid phase, assuming that a thin film surrounding the particle provides the resistance to mass transfer, is expressed as follows:

$$\frac{dC_t}{dt} = K_c a \times (C^* - C_t) \quad (4)$$

Where, a is the specific area of the liquid-solid interface (cm^2/cm^3) and K_c is the mass transfer coefficient of *C. juncea* oil in the liquid phase which is equivalently denoted as the rate constant k (min^{-1}). Thus, Eq. (4) can be written as follows:

$$\frac{dC_t}{dt} = k \times (C^* - C_t) \quad (5)$$

The integrated form of Eq. (5), considering k and C^* remaining constant during the entire process of extraction, along with the initial condition of $C = C_0 = 0$ at $t = 0$ (since pure solvent is used initially), gives the following,

$$\ln \frac{C^* - C_t}{C^*} = -k \times t$$

$$\text{Therefore, } C_t = C^* (1 - e^{-k.t}) \quad (6)$$

Eq. (6) represents variation of *C. juncea* oil concentration with time because of washing and diffusion until equilibrium concentration (C^*) is reached which is expected when $t \rightarrow \infty$.

Therefore, for diffusion and washing processes,

$$C_{t1} = C_1^* (1 - e^{-k_1 t}) \quad (7)$$

$$C_{t2} = C_2^* (1 - e^{-k_2 t}) \quad (8)$$

Where, subscripts 1 and 2 denote washing and diffusion, respectively. It is assumed that $k_1 > k_2$. The total oil yield is represented by;

$$C_t = C_{t1} + C_{t2} \quad (9)$$

$$C^* = C_1^* + C_2^* \quad (10)$$

Combining Eq. (7) to Eq. (10), Eq. (6) is simplified as;

$$C_t = C^* - C_1^* \times e^{-k_1 t} - C_2^* \times e^{-k_2 t} \quad (11)$$

On dividing Eq. (11) by C^* , one obtains

$$\frac{C_t}{C^*} = 1 - f \times e^{-k_1 t} - (1 - f) \times e^{-k_2 t} \quad (12)$$

Where, $f = C_1^*/C^*$ and $(1 - f) = C_2^*/C^*$ are constants representing the fractions of oil leached into the solution by washing and diffusion, respectively.

Using material balance of oil extraction at any instance and at the equilibrium condition give;

$$V \times C_t = M \times q \quad (13)$$

and,

$$V \times C^* = M \times q_\infty \quad (14)$$

where, V is the volume of liquid phase (mL), M is the mass of crushed seed (gm.), q is the oil yield (gm./gm) at any time t and q_∞ is the oil yield at equilibrium.

Considering Eqs. (12), (13) and (14), the combined expression for oil yield, as leaching progresses, is given as:

$$q = q_\infty [1 - f \times e^{-k_1 t} - (1 - f) \times e^{-k_2 t}] \quad (15)$$

Eq. (15) is the *Phenomenological model* of oil extraction (Kostic et al., 2014) from seeds which is also indicated as a *two-site kinetic desorption model* (TSKDM). Previously, this model has been applied

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