

Microbeats Distributions on Tensor Fields

CEBRAİL OZAN OKTAR

Department of History of Science

University of Notr Dame

440 Geddes Hall, University of Notre Dame, Notre Dame, IN 46556

USA

Abstract: In this study, isotropic and anisotropic microbeads were synthesized and characterized in Microbeats Distributions on Tensor Fields Isotropic microbeats materials have identical material properties in all directions at every given point. This means that when a specific load is applied at any point in the x, y or z-axis, isotropic mirobeats materials will exhibit the same strength, stress, strain,hardness.

Anisotropic microbeats materials, also known as “triclinic” materials, are direction-dependent mediums that are made up of unsymmetrical crystalline structures. In other words, the mechanical properties of anisotropic materials depend on the orientation of the material’s body. Each surface reacts differently upon applying the same load to different axes. This implies that if a certain mechanical or thermal property is measured along the x-axis, measurements will differ upon taking it along the y-axis or z-axis. Also, the concentration and the distribution of atoms are different with respect to reference axes. So, as the axis changes, the measurements change as well.

Keywords: Microbeats, isotropy, anisotropy, tensor, adsorption isotherms, magnetic polymers, polymeric microbeads

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1 Introduction

Adsorption isotherm equations, which explain the process at equilibrium conditions, provide an easier solution to complicated problems such as external mass transfer of solute, intraparticle diffusion, and adsorption at sites. Unless extensive data are available, it is impossible to predict the rate-determining step involved in the process. Therefore, the most appropriate method in designing the adsorption systems and in assessing the performance of the adsorption systems is to have an idea on adsorption isotherms. Langmuir and Freundlich models (two-parameter models) are the most commonly used isotherms. Simplicity and easy interpretability are some of the important reasons for extensive use of these models[1,6]. Moreover, linear regression has been frequently used to evaluate the model parameters.

However, transformations of nonlinear isotherm equations to linear forms usually result in parameter estimation error and distort the fit . Thus, a nonlinear method is a better way to obtain the equilibrium isotherm parameters. Most of the published literature had used two or three isotherm models, mainly Freundlich, Langmuir, and Dubinin- Radushkevich. In the present work, an attempt has been made to test most of the available isotherm models with the sorption data obtained. Considering these, the efficacy of h-mag-poly(EGDMA–VIM) for the removal of Cr(VI) was assessed using the best fit of single parameter model developed by Henry , two parameter models by Freundlich , Langmuir , Dubinin-Radushkevich (DR) , Temkin and Halsey , three-parameter models by Redlich-Peterson , Sips , Khan , Radke-Prausnitzr , Toth and Koble-Carrigan , four- and

five-parameter models by Fritz and Schlunder isotherms in their nonlinear form[1].

2 Polymeric microbeads

Polymeric microbeads with different properties can be easily be produced and converted into specific adsorbents by introducing different metal-complexing ligands. Thus, metal-complexing ligands in polymeric microbeads such as dithiocarbamate, dithizone, vinyl pyridine , phenylenediamine , chitosan, vinyl imidazole , diethylenetriamine, N-methacryloylhistidine, poly(ethyleneimine) , salicylaldoxime , tannic acid and vinyl triazole have been used for the removal of heavy metal ions.

Magnetic polymeric beads are currently enjoying a fairly ample range of applications in many fields including biotechnology, nanotechnology and biochemistry . Their magnetic feature makes sampling and collection of waste water (or pollutants) easier and faster. Magnetic microbeads are commonly manufactured from polymers since they have a variety of surface functional groups which can be tailored to use in specific applications. Different polymeric magnetic beads are used in the removal of Cr(VI) ions applications[1,6].

3 Microbeads Distributions on Tensor Fields

The variation of anisotropic properties such as amount of adsorption q_e at equilibrium can conveniently be illustrated by a "representation surface".

In many cases this is an ellipsoid.

Suppose a three-dimensional amount of adsorption $q_e = \psi$ gradient, at equilibrium $\text{grad}q_e = \text{grad}\psi$ or $\nabla q_e = \nabla\psi$, lies along a direction specified by direction cosines l, m, n , where, for

l is the cosine of the angle between the x -axis and the amount of adsorption gradient vector $\nabla(q_e)_x = \nabla\psi_x$ at equilibrium.

m is the cosine of the angle between the y -axis and the amount of adsorption gradient vector $\nabla(q_e)_y = \nabla\psi_y$ at equilibrium.

n is the cosine of the angle between the z -axis and the amount of adsorption gradient vector $\nabla(q_e)_z = \nabla\psi_z$ at equilibrium.

Then the components of the amount of adsorption gradient parallel to the principal axes will be at equilibrium:

$$\nabla(q_e)_x = (\nabla q_e)l = (\nabla q_e)\cos\theta_x(1)$$

$$\nabla(q_e)_y = (\nabla q_e)m = (\nabla q_e)\cos\theta_y(2)$$

$$\nabla(q_e)_z = (\nabla q_e)n = (\nabla q_e)\cos\theta_z(3)$$

Or

$$\nabla\psi_x = (\nabla\psi)l = (\nabla\psi)\cos\theta_x(4)$$

$$\nabla(\psi)_y = (\nabla\psi)m = (\nabla\psi)\cos\theta_y(5)$$

$$\nabla(\psi)_z = (\nabla\psi)n = (\nabla\psi)\cos\theta_z(6)$$

The components of the adsorption flux at equilibrium are:

$$j_x = k_1(\nabla q_e)l = j_x = k_1(\nabla\psi)l(7)$$

$$j_y = k_2(\nabla q_e)m = j_y = k_2(\nabla\psi)m(8)$$

$$j_z = k_3(\nabla q_e)n = j_z = k_3(\nabla\psi)n(9)$$

or

$$j_x = k_1(\nabla q_e)\cos\theta_x = j_x = k_1(\nabla\psi)\cos\theta_x(9)$$

$$j_y = k_2(\nabla q_e)\cos\theta_y = j_y = k_2(\nabla\psi)\cos\theta_y(10)$$

$$j_z = k_3(\nabla q_e)\cos\theta_z = j_z = k_3(\nabla\psi)\cos\theta_z(11)$$

where k_1, k_2, k_3 are the values of adsorption conductivity along the principal axes, x, y, z are called the principal values at equilibrium.

4 Derivation of the anisotropy on ellipsoid

Hence, resolving back along the direction of the adsorption gradient at equilibrium, the adsorption flux at equilibrium is:

$$j_H = j_x l + j_y m + j_z n = (\nabla q_e)(k_1 l^2 + k_2 m^2 + k_3 n^2)(12)$$

$$j_H = j_x l + j_y m + j_z n = (\nabla\psi)(k_1 l^2 + k_2 m^2 + k_3 n^2)(13)$$

or

$$j_H = j_x \cos\theta_x + j_y \cos\theta_y + j_z \cos\theta_z = (\nabla q_e)(k_1 \cos^2\theta_x + k_2 \cos^2\theta_y + k_3 \cos^2\theta_z)(14)$$

$$j_H = j_x \cos\theta_x + j_y \cos\theta_y + j_z \cos\theta_z = (\nabla\psi)(k_1 \cos^2\theta_x + k_2 \cos^2\theta_y + k_3 \cos^2\theta_z)(15)$$

Thus the value of the adsorption conductivity, k_{lmn} defined by

$$k_{lmn} = \frac{j_H}{\nabla q_e}(16)$$

or

$$k_{lmn} = \frac{j_H}{\nabla\psi} \text{ at equilibrium.}$$

is related to the principal values and the directional cosines by

$$k = k_1 l^2 + k_2 m^2 + k_3 n^2 \quad (17)$$

$$k = k_1 \cos^2 \theta_x + k_2 \cos^2 \theta_y + k_3 \cos^2 \theta_z \quad (18)$$

$$\cos \theta_x = l = \frac{x}{r} \quad (19)$$

$$\cos \theta_y = m = \frac{y}{r} \quad (20)$$

$$\cos \theta_z = n = \frac{z}{r} \quad (21)$$

Substituting in our equation for k gives:

$$k = \frac{k_1 x^2}{r^2} + \frac{k_2 y^2}{r^2} + \frac{k_3 z^2}{r^2} \quad (22)$$

$$k = \frac{1}{r^2} (k_1 x^2 + k_2 y^2 + k_3 z^2) \quad (23)$$

Setting

$$r = \frac{1}{\sqrt{k}} \quad (24)$$

then

$$k_1 x^2 + k_2 y^2 + k_3 z^2 = 1 \quad (25)$$

If all the principal values are positive as they must be for adsorption conductivity at equilibrium, then this equation describes the surface of an ellipsoid. The general equation of an ellipsoid with semi-axes a, b, c is:

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad (26)$$

Thus for this representation ellipsoid, the semi-axes are:

$$\frac{1}{\sqrt{k_1}}, \frac{1}{\sqrt{k_2}}, \frac{1}{\sqrt{k_3}} \quad (27)$$

The radius of this ellipsoid in a general direction is equal to the value of $\frac{1}{\sqrt{k}}$ in that direction. Thus the value of k in a particular direction - the ratio of the component of the adsorption flow at equilibrium in that direction to the magnitude of the adsorption gradient at equilibrium in that direction - can easily be calculated from the radius in that direction.

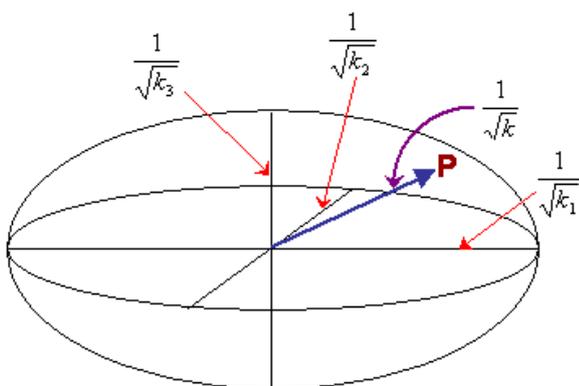


Fig.1 Ellipsoid Anisotropic Microbeats Distributions

5 Different possible contributions to the surface stress

When the interface is deformed, different stresses can arise at the interface.

The surface stress is defined as

$$\sigma = \sigma_{\alpha\beta}(\Gamma)I + \sigma_e \quad (28)$$

where σ is the surface stress tensor, $\sigma_{\alpha\beta}(\Gamma)$ is the scalar surface tension between two phases α and β (with a being the fluid phase and b the air phase), I is a 2×2 identity tensor, Γ is the surface concentration and the σ_e deviatoric surface stress tensor. Capillarity will create gradients in bulk pressure when differences in curvature occur. The surface tension will depend on the concentration of the surface active species, and hence the surface tension may vary in time due to adsorption-desorption kinetics when the area of an interface is suddenly changed.

However, it should be remarked that an isotropic change in surface tension shall not lead to lateral stresses. Rather, spatial variations (in x, y, z) in surface tension are required for this, as they will induce Marangoni stresses. Finally, the response of interfacial microstructures to deformation may give rise to the occurrence of deviatoric stresses of intrinsic rheological origin. We will demonstrate that for the experimental conditions here, neither capillarity nor the adsorption dynamics will play a role.

We expect either the rheological response of the interface or Marangoni stresses (or both) to affect the flow.

$$\sigma = \sigma_{\alpha\beta}(\Gamma(t))I + \sigma_e \quad (29)$$

$\sigma_{\alpha\beta}(\Gamma(t))$ is Gibbs Elasticity what is Adsorption/Desorption

$$\sigma = \sigma_{\alpha\beta}(\Gamma(t, x, y, z))I + \sigma_e \quad (31)$$

$\sigma_{\alpha\beta}(\Gamma(t, x, y, z))$ is Marangoni stresses

$$\sigma = \sigma_{\alpha\beta}(\Gamma(t))I + \sigma_e$$

$\sigma_{\alpha\beta}$ is Capillarity

σ_e is deviatoric stresses intrinsic rheological material function

6 As amount of adsorption at equilibrium on Tensor Fields

Let

$$\sigma = \sigma_{\alpha\beta}(\Gamma)I + \sigma_e$$

where σ is the surface stress tensor, $\sigma_{\alpha\beta}(\Gamma)$ is the scalar surface tension between two phases α and β (with a being the fluid phase and b the air phase), I is a 2×2 identity tensor Γ is the surface concentration and the σ_e deviatoric surface stress tensor and as amount of adsorption at equilibrium q_e with as amount of desorption at equilibrium q_d

$$\sigma_{\alpha\beta}(\Gamma(t)) = \frac{q_e}{q_d}(32)$$

$$\sigma = \sigma_{\alpha\beta}(\Gamma(t))I + \sigma_e$$

$$\sigma = \frac{q_e}{q_d}I + \sigma_e(33)$$

$$\sigma q_d = q_e I + \sigma_e q_d(34)$$

As amount of adsorption at equilibrium on Tensor Fields

$$(\sigma - \sigma_e)q_d = q_e I(35)$$

7 Single and three-parameter adsorption isotherm models on Tensor Fields

If we apply as amount of adsorption at equilibrium on Tensor Fields for single and three-parameter adsorption isotherm models

For Henry equation

$$q_e = K_{HE}C_e(36)$$

$$(\sigma - \sigma_e)q_d = q_e I(37)$$

$$(\sigma - \sigma_e)q_d = (K_{HE}C_e)I(38)$$

For Freundlich equation

$$q_e = K_F(C_e)^{\frac{1}{n}}(39)$$

$$(\sigma - \sigma_e)q_d = q_e I(40)$$

$$(\sigma - \sigma_e)q_d = \left(K_F(C_e)^{\frac{1}{n}}\right)I(41)$$

For Langmuir equation

$$q_e = \frac{(q_m K_L C_e)}{(1 + K_L C_e)}(42)$$

$$R_L = \frac{1}{(1 + K_L C_e)}(43)$$

$$(\sigma - \sigma_e)q_d = q_e I(44)$$

$$(\sigma - \sigma_e)q_d = \left(\frac{q_m K_L C_e}{(1 + K_L C_e)}\right)I(45)$$

For Dubinin-Radushkevich equation

$$q_e = q_m \exp(-\beta e^2)(46)$$

$$e = RT \ln \left(1 + \frac{1}{C_e}\right)(47)$$

$$(\sigma - \sigma_e)q_d = q_e I(48)$$

$$(\sigma - \sigma_e)q_d = (q_m \exp(-\beta e^2))I(49)$$

For Temkin equation

$$q_e = \ln(K_{Te} C_e)_{Te}^B(50)$$

$$(\sigma - \sigma_e)q_d = q_e I(51)$$

$$(\sigma - \sigma_e)q_d = (\ln(K_{Te} C_e)_{Te}^B)I(52)$$

For Halsey equation

$$q_e = \left(\frac{K_H}{C_e}\right)^{\frac{1}{n_H}} (53)$$

$$(\sigma - \sigma_e)q_d = q_e I (54)$$

$$(\sigma - \sigma_e)q_d = \left(\frac{K_H}{C_e}\right)^{\frac{1}{n_H}} I (55)$$

8 Conclusions

An isotropic microbead material is highly formable and may take any shape. Since the properties of its microcomponents are the same in any orientation, its behaviour is also highly predictable.

Metals, glasses, most liquids, and polymers are examples of isotropic materials.

Isotropic microbeads materials have identical material properties in all directions at every given point.

Anisotropic microbeads materials, also known as “triclinic” materials, are direction-dependent mediums that are made up of unsymmetrical crystalline structures.

Metals, on the other hand, besides generally having relatively high strength, exhibit high thermal and wear resistance. Any objects used on a daily basis employ one or other forms of metal.

As amount of adsorption at equilibrium and Microbeads distributions on Tensor Fields

$$(\sigma - \sigma_e)q_d = q_e I$$

References

- [1] A. Kara et al.,” Synthesis and Characterization of Barium Ferrite Containing Magnetic Affinity Microbeads and Isotherm Analysis of Cr(VI) Ions Adsorption from Aqueous Solutions, *Hacettepe Journal of Biology and Chemistry*, 2014, 42 (3), 299–312.
- [2] G. Halsey, Physical adsorption on non-uniform surfaces, *Journal of Chemical Physics*, 16 (1948) 931.
- [3] O. Redlich, D.L. Peterson, A Useful Adsorption Isotherm, *Journal of Chemical Physics*, 63 (1959) 1024.
- [4] R. Sips, On the structure of a catalyst surface, *Journal of Chemical Physics*, 16 (1948) 490.
- [5] A. Kara, L. Uzun, N. Beşirli, A. Denizli, Poly(ethylene glycol dimethacrylate-n-vinyl imidazole) beads for heavy metal removal, *Journal of Hazardous Materials*, 106B (2004) 93.
- [6] A. Kara, B. Erdem, Synthesis, characterization and catalytic properties of sulfonic acid functionalized magnetic-poly(divinylbenzene-4-vinylpyridine) for esterification of propionic acid with methanol, *Journal of Molecular Catalysis A: Chemical*, 349 (2011) 42.

